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XIV.—CAMPHORIC ACID.

FIFTH PAPER.

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Synthesis of the Neighboring Xylic Acid.

In my last paper,[1] experiments of Mr. E. B. Harris and myself were described which led to the preparation of a ketone, by simple reactions, from cis-campholytic acid (the isolauronolic acid of Koenigs and Hoerlin[2]). The oxime of this ketone melted at 104°.[3] By an error in our thermometer we were led to think that the melting-point of this oxime approaches closely to that of the oxime of dimethyl-(1,3)-cyclohexanone(2) as given by Kipping,[4] and the identity of the

[1] This JOURNAL, **18**, 685.

[2] Ber. d. chem. Ges., **26**, 814; **27**, 3467; This JOURNAL, **17**, 429.

[3] The melting-point is given in our paper as 112°-113°. The determination was made with an Anschütz thermometer graduated in fifths of a degree and supposed to be very accurate. In using it later I was led to question its accuracy, and on testing it found, to my surprise, that its record was 8°.5 too high at the boiling-point of water, and 5° too high at the boiling-point of glacial acetic acid. The melting-point of the oxime of the ketone derived from cis-campholytic acid was, therefore, 104°, instead of 112°-113°, as given. That of the oxime of dimethyl-(1,3)-cyclohexanone(2) was 115°-117° instead of 120°-122°, as given in our paper.

The melting-point of α-bromdihydro-cis-campholytic acid should also be 124°-125° instead of 129°-130°, as given in the same paper (This JOURNAL, **18**, 689). The other six thermometers of the set were found, on testing, to be remarkably accurate and the other melting-points and boiling-points of the paper are correct.

[4] J. Chem. Soc., **67**, 357 (1895).

two seemed possible. Both Kipping[1] and Zelinsky[2] have since given the melting-point of the pure oxime as 118°–119° and the agreement in melting-points is now known to be illusory. Since, however, Zelinsky[3] gave the melting-point of the oxime at first as 104°–105°, and since both he and Kipping[4] have obtained evidence of a stereomeric form melting at a much lower temperature, it is still quite possible that the oxime of the ketone from cis-campholytic acid is a mixture of stereomers and that the ketone is in reality dimethyl-(1,3)-cyclohexanone (2). In any case it has seemed worth while to obtain positive evidence on the point by the synthesis of the Δ^1-tetrahydroxylic acid, $C_6H_7\begin{cases}CH_3 & (1)\\ CO_2H & (2)\\ CH_3 & (3)\end{cases}$, and a comparison of its properties with those of cis-campholytic acid. The tetrahydro acid has not yet been obtained but the synthesis of the corresponding xylic acid has been effected and the remaining steps of the synthesis are reasonably certain. As it will be some time, however, before the work can be completed it seems desirable to give an account now of the portion already finished.

The neighboring xylic acid was obtained by Jacobsen[5] some years ago by melting the sodium salt of the 2-sulphonic acid of metaxylene with sodium formate. It is evident from the properties of the acid to be described in this paper that Jacobsen's acid was quite impure. He obtained it in very small amount and gives no analysis. His method of preparation appears so unpromising that no attempt to use it has been made.

Nitrile of the Neighboring Xylic Acid.

This nitrile appears to have been obtained, also, in impure condition by Jacobsen.[6]

I have prepared[7] the nitrile from the 2-aminometaxylene by Sandmeyer's reaction. The necessary xylidine was first

[1] Chem. News, **73**, 44.
[2] Ber. d. chem. Ges., **30**, 1543.
[3] Ber. d. chem. Ges., **28**, 781.
[4] *Loc. cit.*
[5] Ber. d. chem. Ges., **11**, 21.
[6] *Loc. cit.*
[7] A portion of this work was done by Mr. W. E. Burk. See This JOURNAL, **18**, 692.

obtained by nitrating metaxylene,[1] reducing the dinitroxylenes with alcoholic ammonium sulphide, separating the two nitroxylidines with warm gasoline or ligroïn, eliminating the amino group and reducing the 2-nitroxylene with tin and hydrochloric acid. After separation of the two nitroxylidines by means of gasoline the purification of the 2-nitroxylidine is best effected by crystallization of its chloride, which is moderately soluble in pure water but quite difficultly soluble in hydrochloric acid.

The yield of 2-nitroxylidine was poor and other workers seem to have had the same experience. Our work leads us to think that a rapid nitration of small quantities of xylene at a low temperature would give better results than when the product is left longer in contact with nitrosulphuric acid. An attempt to prepare the 2-nitroxylene by the method of Miolati and Lotti[2] from diaminonitroxylene was not successful, probably because the abstracts[3] of their paper do not give sufficiently full details for practical use.

It was found, later, that the easiest method of obtaining the 2-xylidine in small amounts is from commercial xylidine. The samples which we have examined contain approximately 2 per cent. of the compound. 600 grams of the commercial xylidine were mixed with 150 cc. of glacial acetic[4] acid and the mixture was allowed to stand several hours to cool and crystallize. The crystals were sucked as dry as possible, and then washed with ligroïn till nearly white. These crystals are suitable for the preparation of pure asymmetric acetxylide (see below). The first filtrate and the xylidine recovered from the washings were washed with a strong solution of sodium hydroxide to remove acetic acid. It was then converted into the neutral sulphate by treatment with the calculated amount of dilute sulphuric acid. From the more soluble portions of the sulphates[5] 100 grams of xylidine were obtained. To this were added 13 grams of xylidine recovered after the preparation of pure asymmetric acetxylide as described

[1] Grevingk: Ber. d. chem. Ges., **17**, 2423. [2] Gaz. chim. Ital., **27**, I, 293–99.
[3] Centralblatt, 1897, I, 1123; J. Chem. Soc., **72**, 560.
[4] Linebach: Ber. d. chem. Ges., **20**, 871.
[5] Nölting and Pick: Ber. d. chem. Ges., **21**, 3150.

below. The whole was mixed with 200 cc. of glacial acetic acid and boiled at such a rate that three-fourths of the acid distilled away in three hours. On fractioning the remainder, 34 grams of xylidine, boiling at 200°–250°, were obtained from the portion boiling below 300°. This was converted into acetxylide by means of acetic anhydride. On boiling the acetxylide obtained with four times its weight of 25 per cent. sulphuric acid for an hour there crystallized from the solution, on cooling, 12.6 grams of the neighboring acetxylide. This melted at 176°–176°.5, and was practically pure. A small additional amount may be recovered from the mother-liquors. In another case 1150 grams of the xylidine gave 23 grams of the acetxylide, melting at 178°–179°.

The acetxylide was saponified by boiling 20 grams of it with 30 cc. of concentrated sulphuric acid and 16 cc. of water for three hours.

The nitrile was prepared from the xylidine by Sandmeyer's reaction, as usual, using the diazo compound prepared in a solution in hydrochloric acid. In the earlier experiments the attempt was made to saponify the liquid which distilled with water vapor without further purification. Boiling for several days with alcoholic potash[1] appeared to convert it partly into the amide, but, after crystallization, treatment of the product with concentrated sulphuric acid and sodium nitrite[2] gave an acid the composition of which, on analysis, did not agree with that of xylic acid. After several ineffectual attempts to prepare the xylic acid by other methods the nitrile was again prepared and it was found that by fractioning the oil at first obtained it could be separated into two portions. The lower-boiling portion contained a considerable amount of chlorxylene. The higher-boiling portion solidified on cooling and was crystallized from ligroïn. This proved to be the pure nitrile.

The *nitrile* crystallizes from ligroïn in white prisms or thick needles. These are easily soluble in warm ligroïn, difficultly soluble in cold. It is easily soluble in alcohol and ether. It sublimes easily. The crystals melt at 89°.

[1] V. Meyer: Ber. d. chem. Ges., **29**, 834.
[2] Bouveault: Bull. Soc. Chim., **9**, 368.

0.1082 gram of the nitrile gave 11.85 cc. of nitrogen at a temperature of 25°.5 and a pressure of 647 mm.

	Calculated for $C_8H_{13}-CN<^{CH_3}_{CH_3}$.	Found.
N	10.69	10.71

It is probable that the nitrile could be saponified by the method of Bouveault[1] as modified by Sudborough,[2] but, as the corresponding xylic acid has been prepared by another method, no further experiments to that end have been tried.

Attempts to Prepare Hexahydroxylic Acid from Dimethylcyclohexanone.

An attempt was next made to prepare hexahydroxylic acid from dimethyl-(1,3)-cyclohexanone-(2). The necessary dimethylpimelic acid, $CH_2<^{CH_2CH<^{CH_3}_{CO_2H}}_{CH_2CH<^{CH_3}_{CO_2H}}$, was prepared,[3] partly by the method sketched in my last paper,[4] partly by using methylmalonic ester and trimethylene bromide, partly from methyl acetacetic ester and trimethylene bromide.[5] The trimethylene bromide was prepared from trimethylene glycol, partly by means of phosphorus tribromide, partly by mixing it with concentrated hydrobromic acid and distilling slowly, separating the aqueous portion of the distillate from the trimethylene bromide formed and distilling the former again. This latter method proved more satisfactory.

The dimethylpentanetetracarboxylic acid which was obtained as an intermediate product is spoken of in the literature[6] as easily soluble in water. I have found it quite difficultly soluble in cold water, and that it may be easily purified by crystallization from hot water. The pure acid melts

[1] *Loc. cit.* [2] J. Chem. Soc., **67**, 601.

[3] I wish here to express my sincere thanks to Professor A. A. Noyes, who very kindly furnished me with 200 grams of trimethyleneglycol, obtained by fractioning an impure glycerin, for use in preparing the necessary trimethylene bromide. See J. Am. Chem. Soc., **17**, 890.

[4] This JOURNAL, **18**, 694; Perkin: J. Chem. Soc., **51**, 241; Perkin and Prentice: *Ibid*, **59**, 823, 829.

[5] Kipping and Mackenzie: *Ibid*, **59**, 577; Kipping: Chem. News, **74**, 279.

[6] Perkin and Prentice: *Loc. cit.* The melting-point is there given as 200°–205°.

with decomposition at 210°–211°, when heated quickly. The acid was analyzed as follows:

0.2451 gram of the acid gave 0.1288 gram H_2O, and 0.4264 gram CO_2.

	Calculated for $CH_3\langle CH_2-C<^{CH_3}_{(CO_2H)_2} \atop CH_2-C<^{(CO_2H)_2}_{CH_3}$.		Found.
C_{11}	132	47.83	47.44
H_{18}	16	5.80	5.84
O_8	128	46.37	....

Dimethylcyclohexanone was prepared from the dimethylpimelic acid by distilling with an excess of lime.

From the ketone an attempt was, at first, made to prepare and saponify the cyanhydrine. This proving unsuccessful, another portion of the ketone was reduced to dimethylcyclohexanol by means of moist ether and sodium,[1] and from the alcohol the bromide was prepared by warming with concentrated hydrobromic acid in a sealed tube.[2] The bromide was boiled for two hours with potassium cyanide in alcoholic solution (80 per cent.) and the resulting cyanide was boiled with alcoholic potash (33 per cent.) for some time. No evidence of the formation of more than mere traces of the desired hexahydroxylic acid could be obtained. It is quite possible that by the use of larger quantities of material, and by a careful study of the conditions, one or both of these methods could be made successful, but the difficulties are so great that the method was abandoned.

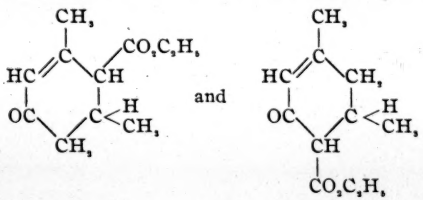
Attempts to Prepare Derivatives of Xylic Acid from Ethylidenediacetacetic Ester.

Some time ago Knoevenagel[3] obtained ethylidenediacetacetic ester,

$$\begin{array}{l} CH_3-CO-CH-CO_2C_2H_5 \\ \qquad\qquad | \\ \qquad CH_3-CH \\ \qquad\qquad | \\ CH_3-CO-CH-CO_2C_2H_5 \end{array} ,$$

[1] Baeyer: Ann. Chem. (Liebig), **278**, 106. [2] *Loc. cit.*, p. 107.
[3] *Ibid*, **281**, 104.

by condensing acetacetic ester with acetaldehyde at a low temperature by use of a small amount of piperidine or diethylamine. When ethylidenediacetacetic ester is heated to 140°–150° for three or four hours with twice its weight of water in a sealed tube, it condenses to a cyclic compound, and loses carbon dioxide and ethyl alcohol. In his first paper[1] Knoevenagel considered that a mixture of two bodies,



of which the second was soluble in a cold dilute solution of sodium hydroxide, is formed by this treatment. In a recent paper,[2] owing to Callenbach's[3] work with similar compounds, he considers it more probable that the mixture consists of a mixture of the ketone and "enol" forms of the second compound. I have, of course, only studied the matter so far as was necessary for the purpose in view, but my work has incidentally proved that the mixture contains the ketone form (or at least a form insoluble in cold dilute sodium hydroxide) of the δ-ketone ester. It has also rendered it probable that the β-ketone ester is present, and I consider it altogether likely that both ketone and "enol" forms of both bodies are formed.

Before the complex nature of the mixture was understood, several attempts were made to reduce the portion insoluble in a cold dilute solution of sodium hydroxide, in the hope of obtaining the corresponding hydroxy-hexahydroxylic acid. Analyses of the products formed demonstrated that a partial reduction was effected, but, as no definite compounds were isolated, further details are unnecessary.

[1] *Loc. cit.*, p. 110. [2] Ann. Chem. (Liebig), **297**, 144.
[3] Ber. d. chem. Ges., **30**, 639.

Next the mixture was converted into derivatives of benzene by methods similar to that by which Knoevenagel converted 3,5-dimethyl-Δ^2-cyclohexenone[1] into the symmetric xylenol.

A mixture of 6.7 grams of the ester, distilled under diminished pressure[2] with 15 cc. of chloroform, was cooled to 0° and a mixture of 1.8 cc. (1 molecule) of bromine with 10 cc. of chloroform was slowly added. In the course of ten or fifteen minutes the bromine was decolorized without appreciable evolution of hydrobromic acid. After about two hours the chloroform was distilled away and the residue heated for from five to ten minutes on the water-bath. The last portions of the chloroform were removed by evacuating the distilling-bulb while still hot. On treating the cold residue with ether, there remained undissolved about 0.6 gram of a white solid which was found, after crystallization from alcohol, to consist of the aromatic hydroxy acid corresponding to the δ-ketone ester.

Dimethyl-(1,3)-phenol-5-methylic-(2) acid as thus obtained is a white powder, difficultly soluble in ether, chloroform, and water, more easily soluble in alcohol. It gives only a slight yellow color with ferric chloride. These properties demonstrate that the carboxyl group is in position (2) and not (4). The acid melts at 253°–254°.

0.1098 gram of the acid gave 0.0607 gram H_2O, and 0.2627 gram CO_2.

	Calculated for $C_6H_2(CH_3)_2(CO_2H)(CH_3)(OH)$.		Found.
C_9	108	65.06	65.25
H_{10}	10	6.02	6.13
O_3	48	28.92	....
	166		

The ethyl ester of dimethyl-(1,3)-phenol-5-methylic acid was found to be present in the ethereal mother-liquors mentioned above, and was purified by crystallization, partly from chloro-

[1] Ann. Chem. (Liebig), **281**, 121.

[2] Experiments with the portion of the distilled ester which was insoluble in cold dilute sodium hydroxide gave practically the same results as when the distilled ester was used directly. It would seem that in this, as in so many other cases, the ketone and "enol" forms pass readily, one into the other.

form, partly from alcohol. It crystallizes from alcohol in plates, from water in needles. It melts at 98°. It gives a yellow color with ferric chloride in alcoholic solution. It is soluble in a solution of sodium hydroxide and precipitated again by carbon dioxide. The ester could not be saponified by long boiling with alcoholic potash, with an aqueous solution of sodium hydroxide, or with hydrobromic acid.

0.1641 gram of the ester gave 0.1071 gram H_2O, and 0.4070 gram CO_2.

	Calculated for $C_4H_3(CH_3)(CO_2C_2H_5)(CH_3)(OH)$		Found.
C_{11}	132	68.04	67.64
H_{14}	14	7.21	7.25
O_3	48	....	....
	194		

Although the amount of the hydroxy acid obtained was small, an attempt was made to reduce it with absolute alcohol and sodium, by the method used by Einhorn and Coblitz[1] for *m*-hydroxybenzoic acid.

A portion of the original acid was recovered unchanged, a considerable portion was converted into a compound soluble in sodium hydroxide and reprecipitated by carbon dioxide, and only a very small amount was converted into an acid more easily soluble in ether than the original acid, and which may have contained some of the hexahydroxy acid desired. The method was evidently hopeless and was abandoned.

Attempts to Prepare Xylic Acid by Means of Acetobromxylene and Acetoiodoxylene.

In accordance with the experiments of Schöpff[2] and of Claus,[3] it would seem that when halogen derivatives of benzene are treated with aluminium chloride and acetyl chloride the acetyl group enters in a position para to the halogen when that position is free. Since, further, the acetyl group is readily introduced into mesitylene and the symmetric

[1] Ann. Chem. (Liebig), **291**, 299. [2] Ber. d. chem. Ges., **24**, 3766.
[3] J. prakt. Chem. [2], **44**, 355.

durene, it would seem probable that a similar treatment of the symmetric bromxylene or iodoxylene would give a compound with the acetyl group ortho to the two methyl groups. From such compounds the neighboring xylic acid could be easily obtained by oxidation and elimination of bromine.

The asymmetric acetxylide required was prepared by boiling the xylidine acetate referred to in the earlier part of this paper with an equal weight of glacial acetic acid for four or five hours, allowing the acetic acid to distil very slowly. 600 grams of the commercial xylidine gave 272 grams of the crude acetate, and this gave 164 grams of the pure acetxylide after one crystallization from strong alcohol, and 16 grams were obtained from the mother-liquors.

Bromxylene was, at first, prepared by the direct bromination of acetxylide, saponification of the bromacetxylide, by boiling with concentrated hydrochloric acid and elimination of the amino group. The bromination was effected partly in solution in glacial acetic acid, with or without the addition of iron, partly in solution in chloroform. In the latter case 19 grams of acetxylide, 50 cc. of chloroform, 50 cc. of water, and 6 cc. (18.6 grams) of bromine were shaken together in a glass-stoppered bottle for half an hour. After saponification with concentrated hydrochloric acid, and separation from dibromxylidine as directed by Genz,[1] the bromxylidine was distilled with water vapor and crystallized from ligroïn. In this way the pure bromxylidine of Genz, melting at 96°–97°, was obtained. The yield was poor, and there was a considerable amount of a compound easily soluble in ligroïn, probably an isomer, formed.

An attempt was at first made to eliminate the amino group by dropping a hydrochloric acid solution of the hydrazine compound into a boiling solution of copper sulphate in accordance with the directions given by Erdmann[1] for metachlorparatoluidine. Instead of the desired bromxylene, chlorbromxylene was formed in considerable amount. A subsequent study of the literature bearing on the case makes it seem that Erdmann's directions are seriously at fault.

[1] Ber. d. chem. Ges., 3, 225.
[2] Anleit. z. Darstellung org. chem. Präparate, p. 71.

4-chlor-2-brommetaxylene,[1] prepared as indicated, crystallizes from alcohol in pearly white leaflets, which melt at 68°. It boils at 244°. It is moderately soluble in alcohol and is slowly volatile with water vapor.

I. 0.1941 gram gave 0.2900 gram AgCl + AgBr, and 0.1876 gram Ag.

II. 0.2509 gram gave 0.3748 gram AgCl + AgBr and 0.2439 gram Ag.

	Calculated for $C_6H_2\begin{cases}(CH_3)_2\\Cl\\Br\end{cases}$.	Found. I.	II.
Cl + Br	52.60	52.59	52.17

In later experiments the amino group of the bromxylidine was eliminated, partly by use of ethyl nitrite and absolute alcohol, partly by treatment of the alkaline diazo solution with an alkaline solution of stannous chloride.[2]

By dissolving the resulting bromxylene in carbon bisulphide, adding aluminium chloride and acetyl chloride and boiling for a short time, then decomposing with water, as usual, an acetobromxylene was obtained which boiled at 275°-278° and solidified in a freezing-mixture. After spreading on porous porcelain and washing with a little ligroïn it melted at 33°. Since the symmetric bromxylene prepared from the symmetric xylidine (see below) gives an acetobromxylene which does not solidify in a freezing-mixture, even on adding a crystal of this compound, and since the asymmetric brommetaxylene gives us no acetyl derivative[3] when treated with aluminium chloride and acetyl chloride, it would seem that the bromxylene obtained from this bromxylidine must be the 2-brommetaxylene. Wroblewski,[4] however, obtained, by treatment of this bromxylene with ethyl bromide and sodium, an ethyldimethylbenzene, which gave, by oxidation, a very small amount of mesitylenic acid and a larger amount of uvitic acid. It would seem from his results, therefore, that this bromxylene is the symmetric form.

[1] For the probable position of the bromine atom see below.

[2] Merz and Effront: Ber. d. chem. Ges., **17**, 2329; Culmann and Gasiorowski: J. prakt. Chem. [2], **40**, 97; R. Friedländer: Ber. d. chem. Ges., **22**, 587.

[3] Schöpff: Ber. d. chem. Ges., **24**, 3769. [4] Ann. Chem. (Liebig), **190**, 215.

The evidence here presented is not altogether satisfactory, and it would not be at all difficult to obtain more positive proof for the position of the groups, but I have not been able to find time to follow the matter further.[1]

Preparation of Symmetric Xylidine.

The symmetric bromxylene next used was prepared from the symmetric xylidine by Sandmeyer's reaction. As I have found the directions given in the literature for the nitration of the asymmetric acetxylide very unsatisfactory,[2] it seems worth while to give the methods which were finally used.

25 grams of acetxylide were dissolved in 50 cc. of warm glacial acetic acid and the solution cooled to about 40°. 10 cc. of a mixture of 15 cc. concentrated sulphuric acid and 25 cc. nitric acid (sp. gr. 1.42) were added and the remainder of the mixture was added in portions of 5 cc. at a time at intervals of ten minutes. The temperature must be watched closely, and if it begins to rise rapidly the flask must be cooled as vigorously as possible under the tap. In several cases the temperature rose, in spite of vigorous cooling, to 80°–90° without serious effect upon the yield. After all of the acid has been added and the mixture has stood for from ten to twenty minutes, the whole was poured into about 300 cc. of water. After filtering and washing, the moist product was saponified by boiling in a tightly covered beaker, for from two to three hours, with 135 cc. of concentrated, commercial hydrochloric acid. After filtering, on a hardened filter, from a small amount of tar, the 5-nitroxylidine was precipitated by the addition of 3 or 4 volumes of water. The 6-nitroxylidine present remains in solution. After filtering and washing, the 5-nitroxylidine may be separated from the water which it contains by melting it in a small covered porcelain dish on the water-bath and allowing it to cool. 98 grams of acetxylide nitrated in this manner, in four portions, gave 69 grams of 5-nitroxylidine.

To eliminate the amino group, 25 grams of the nitroxyli-

[1] Since writing the above I find that Vaubel (Ztschr. anal. Chem., 36, 286) states that on brominating asymmetric acetxylide the bromine enters in position 2 or 6.

[2] Nölting and Forel: Ber. d. chem. Ges., 18, 2677.

dine were dissolved in a mixture of 125 cc. of absolute alcohol and 30 cc. of concentrated sulphuric acid, the mixture was cooled quickly to 0°, and, as soon as possible, to avoid crystallization, the ethyl nitrite generated from 25 grams of sodium nitrite[1] and dried in gaseous form by passing over calcium chloride, was passed into the mixture. After a short time the mixture was heated slowly to boiling and boiled for a few minutes till decomposition was complete. A considerable amount of water was then added and the nitroxylene was distilled with a current of steam. The nitroxylene was warmed on the water-bath for some time with a strong solution of sodium hydroxide to saponify any ethoxynitroxylene formed,[2] and, after cooling and washing, the nitroxylene was crystallized from alcohol. 69 grams of the 5-nitroxylidine gave 39 grams of 5-nitroxylene. This was reduced by warming it on the water-bath for two or three hours, with an upright condenser, after adding 50 grams of powdered iron, 100 cc. of water, and 30 cc. of acetic acid (30 per cent.). After adding an excess of sodium hydroxide and distilling with steam, 28 grams of the symmetric xylidine were obtained.

The xylidine was converted into 5-bromxylene by Sandmeyer's reaction, as usual. The yield was poor.

To prepare the acetobromxylene, 5 grams of the bromxylene, 25 cc. of carbon bisulphide, 5 grams of aluminium chloride, and 5 cc. of acetyl chloride were mixed and boiled with a reversed condenser for three-quarters of an hour. After decomposing with dilute hydrochloric acid and fractioning twice, 3.25 grams of acetobromxylene boiling at 272°–276° were obtained.

4-Aceto-5-brom-1,3-xylene is an oil which does not solidify in a freezing-mixture.

0.1315 gram gave 0.1075 gram AgBr.

0.1225 gram gave 0.1015 gram AgBr.

	Calculated for $C_6H_2\begin{cases}(CH_3)_2\\COCH_3\\Br\end{cases}$.	Found. I.	Found. II.
Br	35.24	34.84	35.14

[1] Wallach and Otto: Ann. Chem. (Liebig), **253**, 251.

[2] Nölting and Forel: Ber. d. chem. Ges., **18**, 2678.

When bromacetoxylene is oxidized with a warm alkaline solution of potassium permanganate, *bromxylylglyoxalic acid*,

is formed. After filtering and acidifying, this separated as an oil and was not further studied. If dilute sulphuric acid is added to the hot solution, without filtering off the oxides of manganese, the glyoxalic acid is oxidized to bromxylic acid. The reaction seems to be general and appears to be a very satisfactory means of obtaining acids from acetyl derivatives of benzene.

Bromxylic acid, , crystallizes from alcohol in long, very fine needles, which melt at 183°–184°. On warming for a short time with zinc dust and ammonia, the bromine is easily removed. The resulting acid was distilled with water vapor and then melted at 126°. It was, therefore, the asymmetric xylic acid, , and this establishes the constitution of the compounds described, as given.

0.1166 gram of acid gave 0.0951 gram AgBr.

	Calculated for	Found.
Br	34.94	34.71

Since the yield in the preparation of the symmetric bromxylene was poor, experiments were also undertaken with the symmetric iodoxylene. The latter was prepared by pouring a diazo solution prepared from the symmetric xylidine, in dilute hydrochloric acid, into an excess of a concentrated solution of potassium iodide, and warming till the decomposition was complete.

Symmetric iodoxylene is an oil which boils at 117° under a pressure of 27 mm. and at 234°–235° under atmospheric pressure.

Acetoiodoxylene, $C_6H_2\begin{cases}CH_3 & (1)\\ CH_3 & (3)\\ COCH_3 & (4)\\ I & (5)\end{cases}$, was prepared by mixing 13.3 grams of iodoxylene with 55 cc. of carbon bisulphide, adding 11 grams of aluminium chloride and then, carefully, 9 cc. of acetyl chloride. The mixture was boiled for half an hour on the water-bath, with reversed condenser, and was then treated with cold dilute hydrochloric acid, as usual. After distilling under diminished pressure 10.8 grams of acetoiodoxylene and 1.85 grams of recovered iodoxylene were obtained. The ketone boils at 171° under a pressure of 25 mm. and at 295°–298°, with some decomposition, under atmospheric pressure. During the boiling of the mixture with aluminium chloride there was some liberation of iodine, and it would seem, from the results of the oxidation, that there was a partial change in the position of the iodine atom. The ketone did not solidify in a freezing-mixture.

0.1528 gram of the ketone gave 0.1319 gram AgI.

0.1379 gram of the ketone gave 0.1186 gram AgI.

	Calculated for $C_6H_2\begin{cases}(CH_3)_2\\ COCH_3\\ I\end{cases}$.	Found. I.	Found. II.
I	46.35	46.64	46.45

If the ketone is oxidized in an ice-cold alkaline solution of potassium permanganate with constant agitation, *iodoxylylglyoxalic acid*, $C_6H_2\begin{cases}(CH_3)_2\\ COCO_2H\\ I\end{cases}$, is formed. After filtering and adding an acid this is precipitated as an oil.

The *barium salt*, $\left(C_6H_2\begin{cases}(CH_3)_2\\ COCO_2\\ I\end{cases}\right)_2 Ba + 2\frac{1}{2}H_2O$, crystallizes on cooling its hot solution. It is quite difficultly soluble even in hot water.

	Calculated.	Found. I.	Found. II.	Found. III.	Found. IV.
$2\frac{1}{2}H_2O$	5.71	5.54	6.07	5.45	5.35

	Calculated for anhydrous salt.	Found. I.	Found. II.	Found. III.
Ba	18.48	18.50	18.06	17.98

If the iodoxylylglyoxalic acid is oxidized by means of manganese dioxide and sulphuric acid, it gives the corresponding iodoxylic acid. This was also obtained, mixed with a bibasic acid, by shaking the ketone, at ordinary temperatures, with an alkaline solution of potassium permanganate, and, after the reduction of the latter was complete, heating on the water-bath and adding dilute sulphuric acid. The mixture of acids obtained was separated by conversion into the barium salts. The salt of the bibasic acid separated on cooling the concentrated solution and was easily purified by recrystallization.

Iodomethylterephthalic acid, $C_6H_2\begin{cases}CH_3 & (1)\\ CO_2H & (2)\\ I & (5)\\ CO_2H & (3)\end{cases}$, obtained from this barium salt, crystallizes from hot water in fine, short needles, which melt at 298°. When the acid was treated with zinc dust and ammonia it gave a difficultly soluble acid which melted at 328°–330° (corr.). The only authorities which I can find[1] give the melting-point of methylterephthalic acid, (*α*-xylidinic acid), as 280°–283°. It was supposed at first, therefore, that the acid obtained must be methylisophthalic acid,[2] which melts at 320°–330°. To make sure, methylterephthalic acid was prepared by oxidizing xylic acid, $C_6H_3\begin{cases}CH_3 & (1)\\ CH_3 & (3)\\ CO_2H & (4)\end{cases}$ (m.p. 126°) with an alkaline solution of potassium permanganate. The acid at first precipitated from the filtered solution melted at about 280°, but by dissolving the acid in ammonia and precipitating the hot, dilute solution with hydrochloric acid and repeating the operation several times, the melting-point rose to 325°–330°. Finally the calcium salt was prepared. This is only moderately soluble in water. The air-dried salt lost 18.58 per cent. of water at 138°, and the anhydrous salt gave 18.05 per cent. Ca. Theory, 18.35 per cent. The acid separated from the calcium salt melted with decomposition at 330°–335°. When zinc chloride was added to the solution of the calcium salt no precipitate was formed but a copious pre-

[1] Fittig and Laubinger: Ann. Chem. (Liebig), **151**, 276; Remsen and Iles: This JOURNAL, **1**, 120.

[2] Claus: J. prakt. Chem. [2], **42**, 509.

cipitate separated on warming and redissolved on cooling. It seems certain, therefore, that pure methylterephthalic acid melts at about 330° and not at 280°-283°, as former observers have stated.

The *barium salt*, $C_6H_2\begin{cases}CO_2>Ba\\CO_2\\CH_3\\I\end{cases} + 6H_2O$, is moderately soluble in cold water, easily soluble in hot. The salt effloresces easily.

	Calculated.	Found.			
		I.	II.	III.	IV.
$6H_2O$	19.66	18.81	18.79	19.39	19.43

I. 0.1986 gram of the anhydrous salt gave 0.1051 gram $BaSO_4$.

II. 0.1976 gram of the salt gave 0.1040 gram $BaSO_4$.

	Calculated.	Found.	
		I.	II.
Ba	31.35	31.15	30.95

The filtrate from the barium salt contained two iodoxylic acids. The copper salt of one of these was precipitated on adding a solution of copper nitrate. The acid was recovered by shaking the salt with dilute hydrochloric acid and ether, and was crystallized from alcohol for analysis.

Iodoxylic acid, $C_6H_2\begin{cases}CH_3 & (1)\\CH_3 & (3)\\CO_2H & (4)\\I & (5)(?)\end{cases}$, crystallizes from alcohol in small granular crystals, which melt at 196°-197°. It is practically insoluble in cold water and very difficultly soluble in hot water. When warmed with zinc dust and ammonia it gave xylic acid, which, after distilling with water vapor, melted at 126°.

0.1310 gram of the acid gave 0.1111 gram AgI.

	Calculated.	Found.
I	43.97	45.80

The *barium salt* is very easily soluble in water.

The *copper salt*, $\left(C_6H_2\begin{cases}(CH_3)_2\\CO_2\\I\end{cases}\right)_2 Cu + nH_2O$ is very diffi-

cultly soluble in water. It contained variable amounts of water (5.28 and 7.57 per cent. in two determinations). The salt was analyzed by dissolving it in alcohol with the addition of some hydrochloric acid, precipitating the copper with hydrogen sulphide and washing the cupric sulphide with alcohol.

0.2240 gram of the dry salt gave 0.0281 gram Cu_2S.

0.3453 gram of the dry salt gave 0.0455 gram Cu_2S.

	Calculated.	Found.	
		I.	II.
Cu	10.36	10.02	10.49

On adding hydrochloric acid to the filtrate from this copper salt a second iodoxylic acid was precipitated. From this a barium salt was prepared and from the crystallized barium salt the acid was again obtained and crystallized from hot water. The acid then melted at 172°–173°. The acid is much more easily soluble in hot water than its isomer. After reduction with zinc dust and ammonia it gave xylic acid melting at 126°. It is evident, therefore, that both iodoxylic acids are derived from the same xylic acid. The iodine is probably ortho to the carboxyl in one and meta in the other. The ortho acid could probably be distinguished by the preparation of an iodoso[1] compound from it, but experiments for that purpose have not been undertaken.

The *barium salt*, $\left(C_6H_2\begin{matrix}(CH_3)_2\\ CO_2\\ I\end{matrix}\right)_2 Ba + 6H_2O$, crystallizes from the concentrated solution in needles which are easily soluble in water.

0.1005 gram of the salt lost 0.0133 gram H_2O at 140°, and gave 0.0297 gram $BaSO_4$.

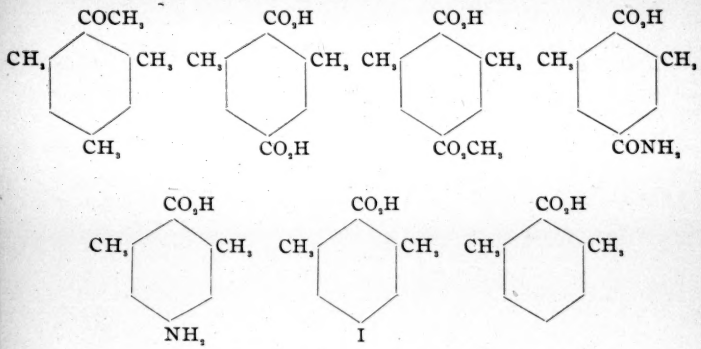
	Calculated.	Found.
$6H_2O$	13.58	13.23
Ba	17.39	17.37

Preparation of the Neighboring Xylic Acid from Acetomesitylene.

The work which has just been described having demonstrated that the acetyl groups of bromacetoxylene and of iodo-

[1] V. Meyer: Ber. d. chem. Ges., **28**, 83; V. Meyer and Kloeppel: *Ibid*, **26**, 1733.

acetoxylene are not in the desired position, experiments were next undertaken with acetomesitylene. These have led to the synthesis of the neighboring xylic acid by means of the following series:



The mesitylene was prepared by the method of Orndorff and Young,[1] slightly modified. As the yield was considerably greater than is reported by others, it seems worth while to give the details. 180 grams of acetone (228 cc.) were placed in a liter distilling-bulb and cooled in ice-water or in a freezing-mixture of ice and commercial hydrochloric acid, 300 grams of concentrated, commercial sulphuric acid (165 cc.) were run in with constant agitation and as rapidly as possible without allowing the temperature to rise above 20°. After sixteen to twenty hours the mixture was heated slowly over a low flame at such a rate that the reaction began in fifteen to twenty minutes. After the reaction had continued for two or three minutes the flame was removed and a moderately rapid current of steam passed in. After three to four minutes longer the receiver was changed and the portions coming over later collected in a separate flask. The distillation with steam was continued till about 200 cc. had passed over. After distilling four portions in this way the oil coming

[1] This JOURNAL, **15**, 256.

over in the second part of the distillations was separated from the aqueous portion of the distillate and was distilled again with water vapor. This effects a partial separation of the mesitylene from high-boiling oils which interfere seriously if the mixed oils are fractioned directly. After 600–800 cc. of the distillate have been collected the residue in the distilling-bulb may be discarded as worthless. The oil which passed over with the steam was mixed with the oil which came over in the first part of the first distillation, washed with a solution of sodium hydroxide, dried with calcium chloride, and fractioned once, with a Ladenburg distilling-bulb, before treatment with sodium. The portion boiling from 150°–210° was collected in 5 portions. The fractionation was then repeated twice with the addition of metallic sodium. In this way 720 grams of the acetone gave 81 grams of mesitylene boiling at 163°–167°, and 4.5 grams 167°–170°. This makes 17.2 per cent. of the theory, while Orndorff and Young[1] obtained 11.5 per cent. of pure mesitylene, and Lucas[2] recently obtained only 13 per cent. (45 grams from 500 grams of acetone) boiling from 160°–170°.

Acetomesitylene was prepared by the method of V. Meyer and Molz.[3] The pure compound boils at 240°–241° with an Anschütz thermometer. Claus[4] gives 235° (uncorr.).

Claus has described[5] an acid which he supposed to be 2,6-dimethylterephthalic acid and which he obtained by oxidizing 2,4,6-trimethylbenzoic acid with potassium permanganate. Jannasch and Weiler[6] have also obtained the 2,6-dimethylterephthalic acid. They obtained it, along with other products, by heating 1,2,3,5-tetramethylbenzene with dilute nitric acid in a sealed tube. I have prepared the acid by the oxidation of acetomesitylene, with the intermediate formation of 2,4,6-trimethylbenzoic acid. At the same time about one-half of the compound is oxidized to the 4,6-dimethylphthalic acid. The properties of the dimethylterephthalic acid which I have obtained agree with those ascribed

[1] *Loc. cit.*
[2] Ber. d. chem. Ges., **29**, 953.
[3] Ber. d. chem. Ges., **30**, 1271.
[4] J. prakt. Chem. [2], **41**, 504.
[5] J. prakt. Chem. [2], **41**, 507.
[6] Ber. d. chem. Ges., **28**, 534.

to the acid of Jannasch and Weiler, but cannot be reconciled with the statement of Claus.

Oxidation of Acetomesitylene.

10 grams of the acetomesitylene were put in a 500 cc. glass-stoppered bottle with 3 grams of sodium hydroxide and 25–30 cc. of water. 20 grams of potassium permanganate were dissolved in 200 cc. of hot water. About 30 cc. of the solution were cooled and added to the contents of the bottle containing the acetomesitylene. The stopper was inserted and the whole was shaken vigorously. The remainder of the permanganate was added in portions of 30–40 cc. at intervals of about five minutes, the vigorous shaking being continued after each addition. The bottle was occasionally cooled so far that the temperature did not rise above 40°–45°. After all of the permanganate had been added and the mixture had been shaken for a short time longer, the contents of the bottle were transferred to a liter flask and heated on the water-bath till the reduction of the permanganate was complete. The solution now contained, chiefly, mesitylglyoxalic acid, $C_6H_2\begin{cases}(CH_3)_3\\ COCO_2H\end{cases}$. 50 cc. of dilute sulphuric acid (25 per cent.) were then added, carefully, with shaking, and the heating was continued for a short time. This causes the oxidation of the mesitylglyoxalic acid to trimethylbenzoic acid. The solution was then cooled, 16 grams of sodium hydroxide were added, and then a solution of 25.6 grams of potassium permanganate in 250 cc. of water was added in two portions at an interval of thirty to sixty minutes. The amount of permanganate used is that calculated for the oxidation of the trimethylbenzoic acid to a bibasic acid and also for the oxidation of the manganese sulphate, formed during the oxidation of the mesitylglyoxalic acid, to manganese dioxide. After two to three hours, or longer, the solution was again warmed on the water-bath till the reduction of the permanganate was complete. 150 cc. of dilute sulphuric acid were then carefully added and, after warming for a short time longer, a strong solution of acid sodium sulphite was added till the oxides of

manganese passed into solution. Most of the dimethylterephthalic acid remains undissolved. A small additional amount separates on cooling. The acid was filtered off, washed, dissolved in ammonia, filtered from a small amount of an indifferent body which is formed, precipitated again with sulphuric acid, and thoroughly washed on a Witts' plate with the pump. 10 grams of the acetomesitylene gave 5 grams of the acid.

2,6-Dimethylterephthalic acid separates, on precipitation, as a very voluminous, amorphous precipitate. It is very difficultly soluble in hot or cold water and is also difficultly soluble in ether. It is easily soluble in alcohol, less soluble in alcohol containing hydrochloric acid.

1,3-Dimethyl-4,5-dimethylic Acid.

About one-half of the acetomesitylene appears to be oxidized to dimethylphthalic acid. This separates from the mother-liquors above, on concentration and cooling. The acid has not been carefully studied, but it is, apparently, moderately soluble in water, difficultly soluble in ether. When heated above its melting-point it is converted into the anhydride.

The *anhydride*, $C_6H_2\begin{cases}CO\\CO\\(CH_3)_2\end{cases}>O$, was purified by dissolving in ether, shaking the ethereal solution with a solution of sodium carbonate, and, after evaporation of the ether, crystallizing from ligroïn. It crystallizes in fine white needles, which melt at 116°.

0.1046 gram gave 0.0444 gram H_2O, and 0.2615 gram CO_2.

		Calculated for $C_6H_2\begin{cases}CO\\CO\\(CH_3)_2\end{cases}>O$.	Found.
C_{10}	120	68.18	68.18
H_8	8	4.54	4.52
O_3	48	....	....
	176		

Acid Methyl Ester of 2,6-Dimethylterephthalic Acid.

Twenty-five grams of dimethylterephthalic acid were put in a flask with 125 cc. of methyl alcohol, and 4 grams of dry hydrochloric acid passed into the mixture. The whole was boiled with reversed condenser for about five hours. After distilling away most of the alcohol, as much as possible of the remainder was removed by evacuating the flask with the filter-pump, while the residue was shaken and gently warmed for a short time. The residue was then used for the preparation of the amide as described below. For analysis the ester was crystallized from water. It crystallizes from water in fine, woolly needles. It crystallizes from alcohol in somewhat coarser needles. It melts at 189°–190°.

0.1571 gram gave 0.0837 gram H_2O, and 0.2618 gram CO_2.

	Calculated for $C_6H_2\begin{cases}(CH_3)_2\\CO_2CH_3\\CO_2H\end{cases}$.		Found.
C_{11}	132	63.46	62.81
H_{12}	12	5.77	5.92
O_4	64	....	....
	208		

According to V. Meyer's law of esterification,[1] the ester group must be in position 5 and not in position 2 with regard to the methyl groups.

To prepare the *amide* corresponding to the ester the residue referred to above was dissolved in 40 cc. of ammonia (10 per cent.), the solution extracted once with ether, and filtered, with care not to increase the volume, and most of the ether in the solution removed by careful exhaustion in a vacuum desiccator. The solution was then nearly saturated with ammonia gas and allowed to stand at summer temperature, 28°–30°, for two or three days. At the end of that time an amount of the ammonium salt of the amide corresponding to 30–40 per cent. of the weight of acid used had separated in crystalline form. This was filtered on a plate covered with asbestos, washed with a little ammonia, dissolved in water, and the pure amide precipitated by hydrochloric acid.

[1] Ber. d. chem. Ges., **27**, 510; **28**, 2773.

2,6-Dimethylterephthalamidic acid, $C_6H_2\begin{cases}(CH_3)_2\\CO_2H\\CONH_2\end{cases}$; crystallizes from water in white needles which melt at 246°. The amide is easily saponified by boiling with a solution of sodium hydroxide and was analyzed in this way.

The distillate from 0.0621 gram of the amide required for neutralization 6.4 cc. of $\frac{1}{20}$-normal HCl.

	Calculated for $C_6H_2\begin{cases}(CH_3)_2\\CO_2H\\CONH_2\end{cases}$.	Found.
N	7.25	7.21

From the ammoniacal mother-liquors mentioned above the dimethylterephthalic acid may be recovered and, by repeating the esterification and treating with ammonia, a new portion can, of course, be converted into the amide.

2,6-Dimethyl-4-aminobenzoic Acid.

3.86 grams of the amide were rubbed thoroughly in a mortar with 45 cc. of an ice-cold solution of sodium hydroxide (10 per cent.). A cold solution of 3.2 grams (1.05 cc.) of bromine in 25 cc. of sodium hydroxide was added carefully with thorough cooling in ice-water. The solution was filtered from a little undissolved amide on an asbestos filter, and the filtrate warmed quickly to near the boiling-point in a water-bath. After cooling, 28 cc. of dilute hydrochloric acid (25 per cent.) were added, the solution was filtered and extracted twice with ether. On adding 15 grams of crystallized sodium acetate the amino acid separated slowly in pure crystalline condition. From the filtrate a small additional amount may be obtained by evaporating in a distilling-bulb under diminished pressure. Evaporation in an open dish causes a decomposition of the acid.

2,6-Dimethyl-4-aminobenzoic acid, $C_6H_2\begin{cases}CO_2H\,(1)\\CH_3\,(2)\\NH_2\,(4)\\CH_3\,(6)\end{cases}$, crystallizes slowly from water in needles which melt with decom-

position at 194°–195°. It is difficultly soluble in water, alcohol, or ether. The *chloride* is also difficultly soluble. When the solution in hydrochloric acid is evaporated to dryness on the water-bath, the acid is almost completely decomposed with the formation of symmetric xylidine. The xylidine was identified by means of its acetyl derivative, melting at 139°.[1] The acetyl derivative prepared from the symmetric xylidine described in the earlier part of this paper melted at exactly the same temperature.

Neighboring Xylic Acid.

From the amino acid, 2,6-dimethyl-4-iodobenzoic acid was prepared by the method given by Wachter[2] for the preparation of *o*-iodobenzoic acid from anthranilic acid. The acid was dissolved in ammonia (10 per cent.), zinc dust added, and the solution warmed for some time on the water-bath. The solution was filtered, acidified, and extracted with ether. The residue left on distilling the ether was distilled with water vapor, the distillate extracted with ether, and the residue from the ethereal solution crystallized from ligroïn.

The *neighboring xylic acid*, $C_6H_3\begin{cases}CH_3\ (1)\\CO_2H\ (2)\\CH_3\ (3)\end{cases}$, crystallizes from ligroïn in white needles which melt at 116°.[3] The acid is more easily soluble in water than its isomers. It is slowly volatile with water vapor, but very little of the acid separates from the distillate. It is very easily soluble in ether, rather difficultly soluble in cold ligroïn.

0.1752 gram of the acid gave 0.1062 gram H_2O and 0.4623 gram CO_2.

	Calculated for $C_6H_3\begin{cases}CH_3\\CO_2H\\CH_3\end{cases}$.		Found.
C_9	108	72.00	71.70
H_{10}	10	6.67	6.73
O_2	32	....	....
	150		

[1] The melting-point is variously given. Wroblewski: Ann. Chem. (Liebig), **207**, 96, gives 144°.5; Thöl: Ber. d. chem. Ges., **18**, 362, gives 138°; Nölting and Forel: *Ibid*, **18**, 2678, give 140°.5.

[2] Ber. d. chem. Ges., **26**, 1744.

[3] Jacobsen gives the melting-point as 97°-99°. Ber. d. chem. Ges., **11**, 21.

The preparation of this xylic acid leaves the main point for which this investigation was undertaken still untouched. Now that a method for its preparation has been discovered, however, it is hoped that the remainder of the work will soon be completed.

ON SOME RELATIONS AMONG THE HYDRATES OF THE METALLIC NITRATES.

By J. H. Kastle.

It is a remarkable fact that by far the greater number of the hydrates of the metallic nitrates contain either 3, 4, 6, 9, or 12 molecules of water, and that in by far the greater number of these salts the number of molecules of water is some simple multiple of three (3). This relation has already been commented upon by other observers. In seeking for some explanation of this relation, it occurred to the writer that these hydrates are to be regarded as addition-products of the base and one of the hypothetical nitric acids;[1] and in this connection it is to be noted that Armstrong[2] in 1891, and again in 1895, in discussing the formation of salts, stated it as probable that the acid and base first unite, and that the salt is formed by an intramolecular change in the addition-product thus produced. There are certainly a great many hydrates of salts known, whose composition is exactly the sum of the acid and the base from which they are derived. The following are a few common examples of hydrates of this type: $CaSO_4.2H_2O$; $BaCl_2.2H_2O$; $HgNO_3.H_2O$, etc. In applying this consideration to the hydrates of the metallic nitrates it is remarkable how simple the relations existing between these compounds appear. According to this supposition we have several different classes of nitrates, which may be regarded as distinct salts of the several hypothetical nitric acids: H_3NO_5, H_3NO_4, HNO_3, N_2O_5, etc.

To the first class belong all of the anhydrous nitrates.

[1] Other observers have found it necessary to assume the existence of salts of the hypothetical nitric acids. For example, in order to account for the lack of color of dilute aqueous solutions of ferric nitrate, Antony and Gigli [Gaz. chim. Ital., **26** (1), 293-311 (1896)] have assumed the existence, in such solutions, of the ferric salts of the acids $H_4N_2O_7$ and H_3NO_5.

[2] Proc. Chem. Soc., 1891, 118.

These compounds may be regarded as addition-products of the anhydride of nitric acid and the metallic oxide, and are probably derived as follows: $M'_2O + N_2O_5 = 2M'NO_3$.

The following anhydrous nitrates are known: KNO_3, $LiNO_3$, $NaNO_3$, $RbNO_3$, $CsNO_3$, $AgNO_3$, $Pb(NO_3)_2$, $Ba(NO_3)_2$, $Sr(NO_3)_2$, $Mg(NO_3)_2$, $TlNO_3$, $Ga(NO_3)_3$, $KAu(NO_3)_4$, $RbAu(NO_3)_4$, $KAu(NO_3)_4$, $KAg(NO_3)_2$, $RbAg(NO_3)_2$.

The second class includes a few nitrates which are probably to be regarded as addition-products of ordinary nitric acid and the metallic base, thus: $M(OH) + HNO_3 = MNO_3.H_2O$. Only a few examples of this class are known. These are the following: $HgNO_3.H_2O$, and $Th(NO_3)_4.4H_2O$.

The third class consists of a considerable number of nitrates of the bivalent and trivalent metals whose composition is identical with that of addition-products of ortho-nitric acid, H_3NO_4, and the metallic base. These salts may be looked upon as deriving as follows:

(1) $M^{II}(OH)_2 + 2H_3NO_4 = M^{II}(NO_3)_2.4H_2O$.

(2) $M^{III}(OH)_3 + 3H_3NO_4 = M^{III}(NO_3)_3.6H_2O$.

The following compounds are to be included in this class:

$Cd(NO_3)_2.4H_2O$,	$Di(NO_3)_3.6H_2O$,
$Ca(NO_3)_2.4H_2O$,	$Fe(NO_3)_3.6H_2O$,
$Sr(NO_3)_2.4H_2O$.	$Tl(NO_3)_3.6H_2O$,
	$Ce(NO_3)_3.6H_2O$,
	$Er(NO_3)_3.6H_2O$,
	$La(NO_3)_3.6H_2O$,
	$Sm(NO_3)_3.6H_2O$,
	$Y(NO_3)_3.6H_2O$.

A number of double nitrates containing very large amounts of water of crystallization would seem also to belong to this class:

$2Ce(NO_3)_3.3CO(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Mg(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Mn(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Ni(NO_3)_2.24H_2O$,
$2Ce(NO_3)_3.3Zn(NO_3)_2.24H_2O$,
$2La(NO_3)_3.3Mg(NO_3)_2.24H_2O$,
$2La(NO_3)_3.3Mn(NO_3)_2.24H_2O$,
$2La(NO_3)_3.3Ni(NO_3)_2.24H_2O$.

These double nitrates may be regarded as deriving, as follows:

$$2M^{III}(OH)_3.3M^{II}(OH)_2 + 12H_2NO_3 = 2M^{III}(NO_3)_3.3M^{II}(NO_3)_2.24H_2O.$$

The fourth class also includes a large number of nitrates of the bivalent and trivalent metals whose composition is that of an addition-product of the acid, H_2NO_3, and the metallic base. These compounds are to be looked upon as deriving as follows:

$$M^{II}(OH)_2 + 2H_2NO_3 = M^{II}(NO_3)_2.6H_2O,$$
$$M^{III}(OH)_3 + 3H_2NO_3 = M^{III}(NO_3)_3.9H_2O,$$
$$M^{IV}(OH)_4 + 4H_2NO_3 = M^{IV}(NO_3)_4.12H_2O.$$

Among the bivalent metals we find the following members of this class of hydrates: $Co(NO_3)_2.6H_2O$, $Fe(NO_3)_2.6H_2O$, $Mg(NO_3)_2.6H_2O$, $Mn(NO_3)_2.6H_2O$, $Ni(NO_3)_2.6H_2O$, $Zn(NO_3)_2.6H_2O$, $Ca(NO_3)_2.6H_2O$.

Among the trivalent metals we find the following: $Al(NO_3)_3.9H_2O$, $Cr(NO_3)_3.9H_2O$, $Fe(NO_3)_3.9H_2O$.

A double nitrate of didymium and nickel is also to be included in this class. This salt has the composition $2Di(NO_3)_3.3Ni(NO_3)_2.36H_2O$, and probably derives as follows: $2Di(OH)_3 + 3Ni(OH)_2 + 12H_2NO_3 = 2Di(NO_3)_3.3Ni(NO_3)_2.36H_2O$.

The most remarkable example of this class of compounds, however, is furnished by the metal thorium. This metal combines with four nitric acid groups, and its ordinary hydrate contains 12 molecules of water of crystallization, $Th(NO_3)_4.12H_2O$. It is to be regarded, therefore, as deriving as follows: $Th(OH)_4 + 4H_2NO_3 = Th(NO_3)_4.12H_2O$.

A fifth class includes a few nitrates which may be regarded as deriving from pyronitric acid, $H_4N_2O_7$, by the direct addition of the metallic base, thus: $M^{II}(OH)_2 + H_4N_2O_7 = M^{II}(NO_3)_2.3H_2O$. To this class belong the following: $Cu(NO_3)_2.3H_2O$, $Ge(NO_3)_2.3H_2O$, $Mn(NO_3)_2.3H_2O$.

Similarly, the octohydrate of thallium nitrate, $Tl(NO_3)_3.8H_2O$, probably derived from the acid, $H_{12}N_2O_{14}$, thus: $Tl(OH)_3 + H_{12}N_2O_{14} = Tl(NO_3)_3.8H_2O$. The acid, $H_{12}N_2O_{14}$,

may be regarded as $3H_2NO_4—H_2O$. Altogether about 70 normal nitrates are described in the literature, and of this number 53 are included in these 5 classes of compounds, and hence come under the rule laid down concerning their composition; *viz.*, that they are to be regarded as addition-products of one of the hypothetical nitric acids and their respective bases. Among these seventy nitrates several are included whose composition is as yet considered doubtful, such as rhodium and zirconium nitrates, $Rb(NO_3)_3.2H_2O(?)$ and $Zr(NO_3)_4.5H_2O(?)$. But even including a number of such doubtful cases, it is certain that 75 per cent. of all the normal metallic nitrates now known conform to the rule under discussion. It can scarcely be doubted, therefore, that these suppositions respecting the composition of this important class of salts contain at least some element of truth.

The many basic nitrates which are known at present have not been included in this discussion, but even these become more intelligible in the light of this hypothesis. Pattison Muir[1] has already pointed out that certain basic nitrates, such as one of the basic lead nitrates, may be regarded as salts of the hypothetical orthonitric acid, H_3NO_4; thus $HPbNO_4$ and $Pb_3(NO_4)_2$ are both known. So, in the same way, if we disabuse our minds of the older notions regarding water of crystallization, the thought suggests itself with reference to the hydrates of the normal nitrates that they are in reality acid salts of complex acids, corresponding in some respects to chlorplatinic acid, and similar compounds, and in such compounds as $Fe(NO_3)_3.9H_2O$ or $H_{18}FeN_3O_{18}$ and $Cu(NO_3)_2.3H_2O$ or $H_6CuN_2O_9$, etc., etc., it is easy to conceive of a further replacement of hydrogen by the metal, and hence, of the formation of so-called basic salts. A few examples, selected somewhat at random from the many basic nitrates described in the literature, are sufficient to indicate that the composition of these salts can be explained by the same general considerations that have already been applied to the interpretation of the normal nitrates. The relation of several of these basic salts to the hypothetical nitric acids is indicated in the following table:

[1] Watts' Dictionary of Chemistry: Muir and Morley, Vol. III, 509.

	Old formulas of basic nitrates.	New formulas of basic nitrates.	Acids of basic nitrates.
1.	$Fe_2N_2O_9$	$2FeNO_4$	$H_4N_2O_8=2H_2NO_4$
2.	$Mg_3N_2O_8$	$Mg_3(NO_4)_2$	$H_4N_2O_8=2H_2NO_4$
3.	$2Hg^{I}_2O.N_2O_5.H_2O$	$H_2Hg^{I}_2N_2O_8$	$H_4N_2O_8=2H_2NO_4$
4.	$2ZnO.N_2O_5.3H_2O$	$H_6Zn_2N_2O_{10}$	$H_{10}N_2O_{10}=2H_5NO_5$
5.	$2Hg^{II}O.N_2O_5.3H_2O$	$H_6Hg^{II}_2N_2O_{10}$	$H_{10}N_2O_{10}=2H_5NO_5$
6.	$3MnO.N_2O_5.3H_2O$	$H_6Mn_2N_2O_{10}$	$H_{10}N_2O_{10}=2H_5NO_5$
7.	$Bi_2O_3.N_2O_5.2H_2O$	$H_5Bi_2N_2O_{10}$	$H_{10}N_2O_{10}=2H_5NO_5$
8.	$10PbO.3N_2O_5.5H_2O$	$H_{10}Pb_{10}N_6O_{30}$	$H_{30}N_6O_{30}=6H_5NO_5$
9.	$Ca(NO_3)_2.Ca(OH)_2.H_2O$	$H_4Ca_2N_2O_9$	$H_8N_2O_9=(2H_5NO_5-H_2O)$
10.	$4ZnO.N_2O_5.2H_2O$	$H_4Zn_4N_2O_{11}$	$H_{12}N_2O_{11}=(2H_5NO_5+H_2O)$
11.	$2Fe_2O_3.N_2O_5.2H_2O$	$H_4Fe_4N_2O_{13}$	$H_{16}N_2O_{13}=(2H_5NO_5+3H_2O)$
12.	$8NiO.2N_2O_5.5H_2O$	$H_{10}Ni_8N_4O_{23}$	$H_{20}N_4O_{23}=(4H_5NO_5+3H_2O)$
13.	$5NiO.N_2O_5.4H_2O$	$H_8Ni_5N_2O_{14}$	$H_{18}N_2O_{14}=(2H_5NO_5+4H_2O)$

The relation of these basic salts to the nitric acids is clearly shown in the above table, and requires no further comment, except to say that it is almost inconceivable that the really fundamental relations existing between these salts could be indicated by means of the formulas usually employed in representing their composition, and which are given in the first column of the table. Compounds 2 and 3 in the table, for example, are both salts of the same acid; *viz.*, H_4NO_4, a fact which is certainly not indicated by a direct comparison of the formulas usually assigned them; and the same may be said of compounds 6 and 7, both of which are salts of H_5NO_5. The fact that in the case of compounds 10, 11, 12, and 13 we are forced to represent their respective acids as hydrates of the acid H_5NO_5 would seem to indicate that the valence of nitrogen towards hydrogen and oxygen is even greater than 5. Indeed the necessity for such an assumption would also seem to exist even among certain hydrates of the normal nitrates. For example, the composition of the double nitrate of cobalt and didymium, $2Di(NO_3)_3.3CO(NO_3)_2.48H_2O$, can only be explained according to these suppositions by assuming it to be a salt of the monohydrate of the acid H_5NO_5. On such an assumption its formation might be accounted for in this way: $2Di(OH)_3.3Co(OH)_2+12H_5NO_5.H_2O=2Di(NO_3)_3.3CO(NO_3)_2.48H_2O$. In such a compound as $H_5NO_5.H_2O$ the nitrogen atom is probably septavalent.

There are only two hydrates that are more complex than those already mentioned. These are the double nitrates, $2La(NO_3)_3.3M(NO_3)_2.69H_2O$ and $2Di(NO_3)_3.3M(NO_3)_2.69H_2O$, which were obtained by Frerichs and Smith[1] in 1876. These hydrates are so complex that exceedingly careful analytical work will be required to determine their composition, and so many revisions of atomic weights have been made since these compounds were investigated that even the theoretical percentage of their components is open to correction. For the present, therefore, these two cases will not be considered.

In conclusion it may be said that, while our knowledge concerning the nature and relations of hydrates is still most unsatisfactory, it is certain that many chemists are coming to believe in the atomic constitution of such compounds just as thoroughly as they admit such a constitution for hydrochloric acid, ammonia, marsh gas, and all the simpler chemical compounds. There are also not a few who are coming to believe that the valence hypothesis in its present shape will have to be modified, perhaps fundamentally, in order to make it applicable to many well-known chemical species which at present it is not sufficient to explain.

In view of these conditions, it is believed that the considerations above advanced are to be regarded as a step in the right direction; and it is the intention of the writer to further develop these and similar ideas when the opportunity presents itself. Certain classes of salts, such as the chlorates, bromates, etc., exhibit many close analogies in composition to the metallic nitrates, and in all likelihood a similar explanation will be found to hold good for the hydrates of these several classes of salts.

STATE COLLEGE OF KENTUCKY,
LEXINGTON, Sept., 1898.

[1] Ann. Chem. (Liebig), **191**, 346–359.

LIQUID AMMONIA AS A SOLVENT.

By E. C. Franklin and C. A. Kraus.

The properties of liquid ammonia as a solvent were made the subject of investigation by G. Gore in the year 1872. In the account of his work, which appeared in the Proceedings of the Royal Society, Gore gives a list of about 350 substances upon which experiments were made. "The investigation was made for the purpose of ascertaining the general solvent properties of liquid ammonia, and to detect any manifest chemical actions between it and the various substances."[1] The tests were made in Faraday tubes, in which the ammonia, generated by heating dry ammoniochloride of calcium, was condensed upon the substance to be studied contained in the second arm of the tube, by refrigeration and its own pressure. The substances examined were for the most part inorganic bodies, including elementary substances and metallic salts, together with a few organic compounds. The results obtained, as stated in an abstract[2] in the Proceedings, are as follows: "The only elements soluble were the alkali metals, also iodine, sulphur, and phosphorus. (Bromine not tried.) The more frequently soluble salts were the nitrates, chlorides, bromides, and iodides. While oxides, fluorides, carbonates, sulphides, and sulphates were generally insoluble. Many saline substances, especially certain chlorides, bromides, iodides, and sulphates absorbed ammonia freely and swelled up greatly but did not dissolve. The behavior of the chlorides of mercury was peculiar. Various compounds of carbon were submitted to the action of the solution of potassium in liquid ammonia, the free potassium disappeared, but no elementary carbon was liberated."

Previous to the work of Gore, Weyl[3] and Seeley[4] had also investigated the action of liquid ammonia on a number of substances. They both, however, gave their attention especially to the blue solution formed by the solution of metallic sodium and metallic potassium in liquid ammonia.

[1] Proc. Roy. Soc., **21**, 140 (1873). [2] *Ibid*, **20**, 441 (1872).
[3] Pogg. Ann., **121**, 601 and 697 (1863); **123**, 350 (1864).
[4] Chem. News, **23**, 169 (1871); Jour. Frank. Inst., **91**, 110 (1871).

These solutions Weyl believed to contain sodammonium, NH_3Na, and potassammonium, NH_3K, or an alloy of the metals with ammonium, NH_4, while Seeley considered them to be simple solutions of the metals in ammonia.

Joannis[1] followed up the study of these sodium and potassium solutions. He investigated the action of a number of substances on sodium and potassium in solution in liquid ammonia, and further, by means of vapor-tension and boiling-point measurements, determined the molecular formulae of the compounds in solution to be $N_2H_6Na_2$ and $N_2H_6K_2$, or $NaH_2N—NH_2Na$ and $KH_2N—NH_2K$, respectively.[2]

The authors in their turn have taken up the study of liquid ammonia with reference to its power as a solvent, and as they have been relieved, by the commercial manufacturers of liquid ammonia, of the necessity of preparing their solvent by the tedious method of Faraday, they have been able to study the behavior of liquid ammonia toward some 500 different substances under much more favorable conditions than were possible at the time Gore carried on his investigations. The results of this work are given below.

Method of Making the Tests.

The ammonia used in these experiments was the ordinary commercial article, such as is furnished by the manufacturers to ice-making plants. For the purpose of carrying out the tests, a quantity of ammonia was drawn from the steel stock cylinder into a medium-sized Dewar test-tube, from which the liquid was removed in quantity to suit the experiment in hand. The transfer of the liquid to the smaller tube in which the test was to be made was easily accomplished by means of a small pipette. The substance to be tested was introduced into this tube, in small quantity at a time and, in case the substance was a solid, in the form of fine powder, and its behavior in contact with the ammonia noted. As nearly as possible the attempt has been made to estimate the solubilities and to express them in accordance with the plan made use of by the editors of the last edition of Watts' Dictionary

[1] Compt. rend., **109**, 900 and 965 (1890); **112**, 337 and 392 (1891); **113**, 795 (1892); **114**, 585 (1892); **116**, 1370 and 1518 (1893); **118**, 713 and 1149 (1894); **119**, 557 (1895).

[2] *Ibid*, **115**, 820 (1893).

of Chemistry. Whether a salt, which from simple inspection appeared to be insoluble, was entirely insoluble or not, was determined by making a measurement of the conductivity of the solution. Those salts indicated in the tables as very slightly soluble formed solutions possessed of distinct conductivity. Salts which produced but a very slight increase in the conductivity of the ammonia are indicated as insoluble. No claim for great accuracy in the estimation of the solubilities of the various salts and more especially of the organic substances can be made, but we believe that in general they are fairly accurate.

General Results.

We have investigated the solubilities of 175 salts, some of which had previously been examined by Gore[1] together with 250 carbon compounds.

Elements.—Of the elements Gore reports the alkali metals, lithium, sodium, potassium, and rubidium, and the non-metals iodine, sulphur, and phosphorus to be soluble in ammonia. Copper is slowly acted on by ammonia, especially in the presence of air. We find caesium and selenium to be soluble also.

Fluorides.—The fluorides are insoluble. Of the 15 fluorides tested by Gore but 3 are reported to be at all soluble.

Chlorides.—The chlorides of the alkali metals are but sparingly soluble, while the chlorides of some of the heavy metals are readily soluble. The chlorides of the alkaline earth metals are practically insoluble. The chlorides of magnesium, calcium, strontium, barium, zinc, cadmium, manganese, cobalt, nickel, and lead, when added to liquid ammonia are rapidly acted on by the solvent, considerable heat being generated, and the salts at the same time undergoing a sort of slaking process.[2] The compact particles of the salts swell up and disintegrate, forming a bulky mass, which, while generally insoluble in ammonia, often readily dissolves in an ammonia solution of ammonium nitrate. The substances thus formed are in all probability the already known addition-products of

[1] *Loc. cit.* [2] Observed also by Gore, *loc. cit.*

the respective salts. That such a compound is formed by the action of liquid ammonia on anhydrous calcium chloride, is shown by the following ammonia determinations:

0.1893 gram substance dissolved in water gave on titration with standard acid solution 0.1002 gram, or 53.00 per cent. ammonia.

0.4735 gram substance lost on ignition, 0.2515 gram, or 53.12 per cent. ammonia.

The calculated amount of ammonia in the compound $CaCl_2.8NH_3$[1] is 55.15 per cent.

Bromides.—Judging from the limited number of bromides available for our tests, the bromides are more readily soluble than the chlorides. They are in all respects similar to the chlorides in their behavior, except that they are somewhat more soluble.

Iodides.—Most of the iodides are very readily soluble. Of the salts tested with a solution of ammonium iodide,[2] only barium and strontium nitrates gave immediate precipitates, and in these cases the crystalline character of the precipitates showed that even these iodides are probably slightly soluble. The iodides of magnesium, zinc, and cadmium (the iodides of calcium, strontium, and barium were not tested) are disintegrated as are the corresponding chlorides and bromides. The products of the action are, however, much more soluble than the compounds formed from the other halides. The iodides of silver, mercury, and lead dissolve so rapidly that the slaking phenomenon is scarcely to be observed.

Sulphates.—The sulphates, including sulphuric acid and ammonium sulphate, are entirely insoluble. Neither can the smallest quantity of finely powdered ammonium sulphate be observed to go into solution, nor does the addition of a quantity of the sulphate of ammonium, sodium, potassium, lead, silver, or mercury, alter the high electrical resistance of the solvent.

Sulphides.—But few sulphides have been tested directly for their solubility. Ferrous sulphide and native lead, antimony

[1] Joannis [Compt. rend., **112**, 337 (1891)] has prepared the compound $BaCl_2.8NH_3$ by the action of liquid ammonia on anhydrous barium chloride.

[2] *Vide* article on "Metathetic Reactions" to appear in the January number of this JOURNAL.

and copper sulphides are insoluble. Ammonium sulphide and native arsenous sulphide are soluble.

Sulphites.—The sulphites are insoluble.

Carbonates.—The carbonates are insoluble.

Oxides and Hydroxides.—The oxides and hydroxides tested were found to be insoluble. Mercuric oxide dissolved readily in a solution of ammonium nitrate, as did also, but less readily, cobalt oxide.

Phosphates.—The orthophosphates, metaphosphates, and pyrophosphates examined were found to be insoluble. The hypophosphites are slightly soluble.

Oxalates.—Ammonium oxalate and oxalic acid are insoluble.

Arsenates.—The only arsenates tested, ammonium arsenate and copper arsenate, are insoluble.

Cyanides.—The cyanides are generally easily soluble.

Cyanates and Sulphocyanates.—These salts are, so far as tested, very easily soluble.

Ferrocyanides and Ferricyanides.—The potassium salts are insoluble.

Nitrates.—All the metallic nitrates tested, with the exception of the nitrate of bismuth, are readily soluble; and even this salt goes into solution on the addition of ammonium nitrate to the solvent.

Nitrites.—The three nitrites tested are very easily soluble.

Paraffin Hydrocarbons.—The paraffin hydrocarbons are very slightly soluble or insoluble. The only members of the group tested, *viz.*, hexane and diisoamyl are not perceptibly soluble.

Halogen Derivatives.—The halogen substitution-products of methane and ethane are all either miscible with ammonia or are readily soluble. Derivatives of the higher hydrocarbons are slightly soluble.

Alcohols.—The lower members of the series, up to and including octyl alcohol, are miscible. Cetyl alcohol is insoluble.

Ethers.—Diethyl ether is miscible. Diamyl ether is slightly soluble.

Polyhydroxy Alcohols.—Glycol and glycerin are miscible

with ammonia. Erythrite, dulcite, and mannite are slightly soluble.

Aldehydes.—The simpler aldehydes and their derivatives are either miscible or easily soluble.

Acids.—The fatty acids and their halogen substitution-products are readily soluble; the solubility decreasing with the higher members of the series. The fatty acids proper are not perceptibly soluble.

Dibasic Acids.—The dibasic acids are insoluble.

Ethereal Salts.—The ethereal salts are readily soluble. The members of the group with the lower molecular weights are miscible, the solubility diminishing with increasing molecular weight.

Compounds Containing Nitrogen.—The nitrils, cyanates, sulphocyanates, the amines, the amido acids, the acid amides and the ureides are generally readily soluble. The secondary amines are less easily soluble than the primary amines, while the one tertiary amine tested, trimethylamine, is miscible.

Hydroxy Acids.—The hydroxymonobasic acids are readily soluble; the hydroxydibasic acids are but slightly soluble.

Sugars.—The sugars are very easily soluble. Cane-sugar in concentrated solution forms a thick syrup.

Aromatic Hydrocarbons.—At atmospheric pressure ammonia dissolves about 10 per cent. of its weight of benzene. Toluene is slightly soluble; the isomeric xylenes and ethylbenzene are much less soluble than toluene, while the higher members of the group are not perceptibly soluble.

Halogen Derivatives.—The halogen derivatives are slightly soluble.

Nitro Derivatives.—The nitro-derivatives are moderately soluble.

Amido Derivatives.—Aniline and the toluidines are very easily soluble. The secondary and tertiary amines are slightly soluble.

Phenols.—The phenols are extremely soluble, as are also such ethers as were tested.

Substituted Phenols.—The nitrophenols and the amidophenols are very easily soluble.

Alcohols.—The two tested are miscible.

Aldehydes.—Such as were tested are very easily soluble.

Acids.—The aromatic monobasic acids are readily soluble.

Substituted Acids.—The halogen, hydroxy, nitro, and amido substitution-products are generally readily soluble.

Dibasic Acids.—The dibasic acids are insoluble.

Ethereal Salts.—The ethereal salts are soluble.

Sulphonic Acids.—Such salts and other derivatives of the sulphonic acids as were tested are soluble.

Acid Amides and Anilides.—Such of these compounds as were tested are readily soluble.

Naphthalene and Derivatives.—But few of the derivatives of naphthalene were tested. Naphthalene itself is slightly soluble. The naphthols and naphthylamines are soluble.

Pyridine and Quinoline.—Pyridine and quinoline are miscible. Isoquinoline is slightly soluble.

Terpenes.—The terpenes are insoluble.

Table of Solubilities of Certain Metallic Salts and Organic Substances in Liquid Ammonia.

The degree of solubility is indicated by the following abbreviations: v. e. sol., very easily soluble; v. sol., very soluble; m. sol., moderately soluble; sl. sol., slightly soluble; v. sl. sol., very slightly soluble; insol., insoluble. Experiments made by Gore are indicated by (G). Tests made by Gore which have been repeated by us are marked (FK).

Ammonium Salts.	
Ammonium arsenate,	insol.
" borate,	sl. sol.
" bromide,	v. sol.
" carbonate, (G)(FK)	insol.
" chloride, (G)(FK)	v. sol.
" chromate,	sl. sol.
" hypophosphite,	m. sol.
" iodide,	v. e. sol.
" molybdate	insol.
" nitrate, (G)(FK)	v. e. sol.
" oxalate,	insol.
" oxalurate,	m. sol.
" phosphate,	insol.
" selenate,	insol.
" sulphate,	insol.
" sulphide,	v. sol.
" sulphocyanate,	v. e. sol.
Ammonium thionurate,	m. sol.
" vanadate, (G)	insol.
Aluminium Salts.	
Aluminium acetate,	insol.
" chloride	insol.
" metal, (G)	insol.
Antimony Salts.	
Antimony potassium tartrate,	insol.
" metal, (G)	insol.
" bromide, (G)	v. sol.
" chloride, (G)	insol.
" fluoride, (G)	insol.
" iodide, (G)	action.
" oxide, Sb_2O_3, (G)	insol.
" oxybromide, (G)	sl. sol.
" oxychloride, (G)	insol.
" sulphide red, (G)	insol.

Antimony sulphide, orange, (G)	insol.
" " black, (G)(FK)	insol.
" fluoride, (G)	insol.

Arsenic Salts.

Arsenic metal, (G)(FK)	insol.
Arsenous oxide, (G)(FK)	insol.
Arsenic acid, cryst., (G)	v. sl. sol.
Arsenous chloride, (G)	action
" iodide, (G)(FK)	action
Realgar, (G)	m. sol.
Orpiment, (G)(FK)	sl. sol.

Barium Salts.

Barium acetate,	v. sl. sol.
" hydroxide,	insol.
" metal, (G)	insol.
" chloride, (G)(FK)	insol.
" nitrate, (G)(FK)	m. sol.
" oxide, (G)	insol.
" sulphate, (G)(FK)	insol.

Bismuth Salts.

Bismuth iodide,	sl. sol.
" oxychloride,	insol.
" nitrate,	sol. on addition of ammonium nitrate
" metal, (G)	insol.
" carbonate, (G)	insol.
" chloride, (G)	m. sol.
" fluoride, (G)	insol.
" hydroxide, (G)	insol.
" sulphide, (G)	insol.

Boron Compounds.

Boron, (G)	insol.
Boric anhydride, (G)	insol.
" acid,	sl. sol.

Cadmium Salts.

Cadmium iodide, (G)(FK)	insol., sl. sol.
" nitrate,	m. sol.
" sulphate,	insol.
" bromide, (G)(FK)	insol.
" carbonate, (G)	insol.
" chloride, (G)(FK)	insol.
" fluoride, (G)	insol.
" sulphide, (G)(FK)	insol.

Calcium Salts.

Calcium acetate,	v. sl. sol.
" bromide,	sl. sol.
" butyrate,	insol.
" carbonate,	insol.
" formate,	insol.
" nitrate,	v. e. sol.
Calcium oxide,	insol.
" phosphate,	insol.
" sulphide,	insol.
" sulphite,	insol.
" metal, (G)	insol. white coating formed.
" chloride, (G)(FK)	insol.

Caesium Salts.

Caesium metal,	v. sol.
" alum,	insol.

Cerium Salts.

Cerium chloride, (G)	insol.
" fluoride, (G)	insol.
" nitrate, (G)(FK)	sl. sol.
" oxide, (G)	insol.

Chromium Compounds.

Chromic acid, (G)(FK)	sl. sol.
Chromium chloride, (G)	sl. sol.
" fluoride, (G)	insol.

Cobalt Salts.

Cobalt nitrate,	m. sol. forms a yellow solution.
" oxide,	insol. soluble in ammonium nitrate.
" carbonate, (G)	insol.
" chloride, (G)(FK)	insol.
" fluoride, (G)	insol.
" sulphate, (G)(FK)	insol.

Copper Salts.

Copper metal, (G)(FK)	sl. action
Cupric acetate,	sl. sol.
" arsenate,	insol.
" arsenite,	insol.
" ammonium chloride,	sl. sol.
" formate,	sl. sol.
" nitrate,	v. e. sol.
" sulphate, cryst.,	insol.
" oxide, (G)(FK)	sl. action
" carbonate, (G)(FK)	insol.
" chloride, (G)	insol.
" chromate, (G)	insol.
" ferrocyanide, (G)	insol.
" fluoride, (G)	insol.
" phosphate, (G)	insol.
" sulphate, white, (G)	insol.
" sulphide, (G)(FK)	insol.
Cuprous chloride,	sl. sol.
" iodide,	v. sol.
" oxide, (G)	sl. action
" cyanide, (G)(FK)	m. sol.

Didymium Salts.

Didymium nitrate,	m. sol.

Glucinum Salts.

Glucinum carbonate, (G)	insol.
" chloride, (G)	insol.
" oxide, (G)	insol.
" sulphate, (G)	insol.

Gold Salts.

Gold chloride, (G)	sl. sol.

Iron Salts.

Iron, metallic, (G),	insol.
Ferric bromide,	sl. sol,
" iodide,	v. sol.
" pyrophosphate,	insol.
" sulphate, (G)	insol.
Ferrous lactate,	sl. sol.
" sulphate,	insol.
" sulphide,	insol.
" valerianate,	sl. sol.

Lead Salts.

Lead acetate,	v. sol.
" bromide,	m. sol.
" carbonate,	insol.
" chloride,	sl. sol.
" formate,	m. sol.
" iodide,	v. e. sol.
" nitrate,	v. e. sol.
" oxide (litharge),	insol.
" peroxide,	insol.
" sulphide (galena),	insol.
" tartrate,	insol.
" chromate,	insol.
" metal, (G)	insol.
" oxide, red, (G)(FK)	insol.
" fluoride, (G)	insol.
" iodate, (G)	insol.
" chromate, (G)(FK)	sl. sol.

Lithium Salts.

Lithium benzoate,	v. sol.
" bromide,	m. sol.
" carbonate,	insol.
" chloride,	sl. sol.
" iodide,	v. sol.
" nitrate,	v. e. sol.
" salicylate,	v. sol.
" metal, (G)(FK)	sol.

Magnesium Salts.

Magnesium bromide,	sl. sol.
" iodide,	v. sol.
" carbonate,	insol.
" nitrate,	v. e. sol.
" oxide,	insol.
" phosphate,	insol.
" sulphate,	insol.
" sulphite,	insol.
" metal, (G)	insol.
" basic chloride, (G)	sl. sol.

Manganese Salts.

Manganese carbonate,	insol.
" iodide,	m. sol.
" nitrate,	v. sol.
" metal, (G)	insol.
" chloride, (G)(FK)	insol.
" fluoride, (G)	insol.
" sulphate, (G)(FK)	insol.
" bromide,	insol.

Molybdenum Salts.

Molybdenum metal, (G)(FK)	insol.
" sulphide, (G)	insol.
Molybdic acid, (G)(FK)	insol.

Nickel Salts.

Nickel nitrate,	m. sol.
forms a purplish solution.	
" sulphate,	insol.
" metal, (G)	insol.
" chloride, (G)(FK)	insol.
" fluoride, (G)	insol.
" hydroxide, (G)	insol.
" oxide, (G)	insol.

Osmium Salts.

Osmium metal, (G)	insol.
Osmic acid, (G)	action.

Palladium Salts.

Palladium metal, (G)	insol.
" chloride, (G)	sl. sol.
" sulphide, (G)	insol.

Platinum Salts.

Platinum metal, (G)	insol.
Platinous chloride, (G)	sl. sol.
Platinic chloride, (G)	sl. sol.
" iodide, (G)	v. sol.
Platinum oxide, (G)	insol.

Phosphorus Compounds.

Phosphorus pentoxide,	insol.
Phosphorus, white, (G)(FK)	sol.
" red, (G)(FK)	insol.
Phosphoric acid, glac., (G)	insol.
Phosphorus trichloride, (G)(FK)	action.
" pentachloride, (G)(FK)	action.

Potassium Salts.

Potassium acetate,	sl. sol.
" carbonate,	insol.
" chlorate,	m. sol.
" cyanate,	v. e. sol.
" ethyl sulphate,	v. sol.
" ferricyanide,	insol.
" hydroxide,	insol.
" hypophosphite,	sl. sol.

Potassium iodate,	insol.
" metaphosphate,	insol.
" phenylsulphonate,	m. sol.
" metanitrobenzene-sulphonate,	m. sol.
" sulphate,	insol.
" sulphide,	m. sol.
" pyroantimonate,	insol.
" nitrite,	v. sol.
" nitroprusside,	v. sol.
" sulphite,	insol.
" metal, (G)(FK)	sol.
" bichromate, (G)(FK)	sl. sol.
" bromide, (G)(FK)	m. sol.
" chloride, (G)(FK)	sl. sol.
" chloriridate, (G)	insol.
" chromate, (G)(FK)	insol.
" cyanide, (G)(FK)	m. sol.
" ferrocyanide, (G)(FK)	insol.
" fluozirconate, (G)	insol.
" fluoride, (G)	v. sl. sol.
" iodide, (G)(FK)	v. e. sol.
" nitrate, (G)(FK)	v. sol.
" permanganate (G)(FK)	v. sol.
" silicofluoride, (G)	insol.
" sulphocyanate, (G)(FK)	v. sol.

Mercuric Salts.

Mercuric nitrate,	v. sol.
" fulminate,	v. e. sol.
" sulphocyanate,	v. e. sol.
" chloride, (G)(FK)	m. sol.
" cyanide, (G)(FK)	v. e. sol.
" iodide, (G)(FK)	v. e. sol.
" oxide, yellow, (G)(FK)	insol.
sol. in ammonium nitrate.	
" oxide, red, (G)	insol.
" bromide, (G)	m. sol.
" sulphate, (G)(FK)	insol.
" sulphide, (G)	insol.

Mercurous Salts.

Mercurous acetate, (G)	v. sol.
" iodide,	v. e. sol.
" oxide,	insol.
" chloride, (G)(FK)	v. sol.
" nitrate, (G)(FK)	v. sol.
Mercury metal, (G)	insol.

black precipitates are formed by the action of ammonia on mercurous salts.

Rubidium Salts.

Rubidium chloride,	v. sl. sol.
" metal, (G)(FK)	sol.
" fluoride, (G)	insol.

Silver Salts.

Silver acetate,	sl. sol.
" nitrite,	v. sol.
" thioethylcarbamate,	insol.
" metal, (G)	insol.
" carbonate, (G) (FK)	insol.
" chloride, (G)(FK)	sl. sol.
" chromate, (G)	insol.
" cyanide, (G)(FK)	m. sol.
" fluoride, (G)	sl. sol.
" iodide, (G)(FK)	v. sol.
" iodate, (G)	insol.
" oxide, (G)(FK)	insol.
" peroxide, (G)	insol.
" nitrate, (G)(FK)	v. sol.
" phosphate, (G)	insol.
" sulphate, (G)(FK)	insol.
" vanadate, (G)	insol.
" arsenate, (G)	insol.
" bromide, (G)(FK)	m. sol.

Sodium Salts.

Sodium acetate,	sl. sol.
" bisulphate,	insol.
" bromide,	v. sol.
" carbonate,	insol.
" citrate,	insol.
" chlorate,	v. sol.
" ethyl sulphate,	v. sol.
" formate,	v. sl. sol.
" hydroxide,	insol.
" hypophosphite,	sl. sol.
" iodide,	v. e. sol.
" nitrate,	v. sol.
" nitrite,	v. sol.
" phenylsulphonate,	m. sol.
" propionate,	v. sl. sol.
" pyrophosphate,	insol.
" sulphate,	insol.
" sulphite,	insol.
" tungstate,	sl. sol.
" *o*-xylenesulphonate,	m. sol.
" valerianate,	insol.
" biborate,	insol.
" bromate,	m. sol.
" bichromate,	sl. sol.
" permanganate,	m. sol.
" phosphomolybdate,	insol.
" salicylate,	v. sol.
" thiosulphate,	m. sol.
" metal, (G)(FK)	sol.
" chloride, (G)(FK)	m. sol.

Strontium Salts.

Strontium chloride,	insol.
" nitrate,	v. sol.
" carbonate,	insol.
" sulphate,	insol.
" metal, (G)	insol.

Sulphur Compounds.

Sulphur, (G)(FK)	sol.
" chloride, (G)(FK)	m. sol.
Sulphur iodide,	v. sol.

Thallium Salts.

Thallium chloride,	insol.
" nitrate,	m. sol.
" metal, (G)(FK)	insol.
" fluoride, (G)	insol.
" peroxide, (G)	insol.

Tin Salts.

Stannic chloride, (G)	v. sol.
" oxide, (G)	insol.
Stannous chloride, (G)	part. sol.
" oxide, (G)	insol.
Tin metal, (G)	insol.

Titanium Salts.

Titanic acid, (G)	insol.
Titanium nitrocyanide, (G)	insol.
" oxide, black, (G)	insol.

Uranium Salts.

Uranium fluoride, (G)	sl. sol.
" nitrate, (G)	sl. action
" oxide, (G)	sl. action

Zinc Salts.

Zinc acetate,	m. sol.
" carbonate,	insol.
" chromate,	insol.
" ferrocyanide,	v. sl. sol.
" lactate,	v. sol.
" nitrate,	v. e. sol.
" oxide,	insol.
" phosphate,	insol.
" sulphate,	insol.
" sulphide, (blende)	insol.
" tartrate,	insol.
" bromide, (G)(FK)	v. sl. sol.
" chloride, (G)(FK)	insol.
" cyanide, (G)(FK)	v. sol.
" fluoride, (G)	insol.
" iodide, (G)(FK)	m. sol.

Miscellaneous.

Carbon, charcoal, (G)	insol.
" graphite, (G)	insol.
" bisulphide, (G) (FK)	action
" tetrabromide, (G)	v. sol.
" tetrachloride, (G)(FK)	miscible
" hexachloride, (G)	insol.
Iodine, (G)(FK)	sol.
Iodic acid, (G)(FK)	insol.
Indium metal, (G)	insol.
" black oxide, (G)	insol.
Lanthanum sulphate, (G)	insol.
Niobic acid, (G)	insol.
Osmiridium, (G)	insol.
Selenium, (FK)	sol.
Selenic acid,	insol.
Selenious acid, (G)	insol.
Silicon, cryst., (G)	insol.
" pptd., (G)	insol.
Tungsten, (G)	insol.
Tungstic acid, (G)	insol.
Thorium sulphate, (G)	insol.
Tellurium, (G)(FK)	insol.
Vanadic acid, (G)	insol.
Vanadium nitride, (G)	insol.
Water, (G)(FK)	miscible
Phosgene,	action

Paraffin Hydrocarbons.

Hexane,	insol.
Diisoamyl,	insol.
Paraffin, (G)	insol.

Halogen Derivatives.

Methyl iodide,	miscible
Chloroform, (G)(FK)	miscible
	reaction
Bromoform,	miscible
Iodoform,	v. e. sol.
Ethyl bromide,	m. sol.
" iodide,	m. sol.
Ethylidene chloride,	miscible
Ethylene bromide,	m. sol.
Tribromethane,	v. sol.
Isobutyl bromide,	m. sol.
Amyl bromide,	sl. sol.
Nitrotrichlormethane,	miscible

Alcohols.

Methyl alcohol,	miscible
Ethyl " (G)(FK)	miscible
Propyl "	miscible
Butyl " normal,	miscible
" " iso,	miscible
" " tertiary,	miscible
Pentyl " (G)(FK)	miscible
Heptyl "	miscible
Octyl "	miscible
Cetyl "	insol.

Ethers.

Diethyl ether, (G)(FK)	miscible
Methylal,	miscible
Diamyl ether,	sl. sol.

Polyhydroxy Alcohols.

Ethylene glycol,	miscible
Propylene glycol,	miscible

Glycerine, (G)(FK)	miscible
Erythrite,	v. sl. sol.
Dulcite,	sl. sol.
Mannite,	sl. sol.

Aldehydes.

Acetaldehyde, (G)(FK)	miscible
Paraldehyde,	miscible
Aldehyde ammonia,	m. sol.
Chloral hydrate,	m. sol.
Bromal hydrate,	v. sol.
Chloral cyanhydrate,	v. sol.
Isobutyl aldehyde,	v. e. sol.
Valeric aldehyde,	v. sol.
Heptyl aldehyde,	m. sol.
Glyoxal,	insol.
Pinacone,	v. sol.
Oxymethylene,	insol.

Acids.

Formic acid,	miscible
Acetic acid,	m. sol.
Chloracetic acid,	v. sol.
Dichloracetic acid,	v. sol.
Trichloracetic acid,	v. e. sol.
Bromacetic acid,	v. sol.
Dibromacetic acid,	v. sol.
Propionic acid,	m. sol.
α-Brompropionic acid,	v. sol.
β-Brompropionic acid,	m. sol.
Butyric acid, normal,	m. sol.
Butyric acid, iso,	v. e. sol.
Valeric acid,	m. sol.
Caproic acid,	m. sol.
Oenanthylic acid,	sl. sol.
Caprylic acid,	sl. sol.
Capric acid,	v. sl. sol.
Pelargonic acid,	insol.
Myristic acid,	insol.
Palmitic acid,	insol.
Margaric acid,	insol.
Stearic acid,	insol.

Dibasic Acids.

Oxalic acid,	insol.
Malonic acid,	insol.
Succinic acid, (G)(FK)	insol.
Pyrotartaric acid,	insol.
Diacetsuccinic acid,	v. sol.
Dibromsuccinic acid,	sl. sol.

Ethereal Salts.

Ethyl formate,	miscible
Amyl "	miscible
Ethyl acetate,	miscible
Propyl "	miscible
Isobutyl "	miscible
Amyl "	v. e. sol.
Capryl "	sl. sol.
Methyl propionate,	miscible
Propyl "	v. e. sol.
Amyl "	m. sol.
Methyl butyrate,	miscible
Ethyl "	miscible
Amyl "	sl. sol.
Isobutyl "	m. sol.
Ethyl valerianate,	v. e. sol.
Isobutyl "	m. sol.
Amyl "	sl. sol.
Ethyl caprylate,	sl. sol.
" pelargonate,	sl. sol.
" orthoformate,	miscible
" oxalate,	v. e. sol.
	rapidly forms oxamide.
" malonate,	miscible
" succinate,	miscible
" lactate,	miscible
" tartrate,	miscible
" citrate,	miscible
" carbonate,	miscible
Tributyrin,	miscible
Amyl nitrite,	m. sol.

Cyanides.

Methyl cyanide,	miscible
Ethyl "	miscible
Cyanuric acid,	sl. sol.
Ethyl sulphocyanate,	miscible
Ethyl isosulphocyanate,	v. e. sol.
Paracyanogen, (G)	insol.

Amines.

Methylamine,	miscible
Trimethylamine,	miscible
Diethylamine,	m. sol.
Dipropylamine,	m. sol.
Amylamine,	miscible
Diamylamine,	sl. sol.
Tetramethylammonium iodide,	sl. sol.
Hydroxylaminehydrochloride,	v. sol.

Amido Acids.

Glycocoll,	v. sol.
Amidopropionic acid,	v. sol.
Leucine,	v. sol.
Sarcosine,	v. sol.
Tyrosine,	v. sol.

Acid Amides and Ureides.

Formamide,	v. e. sol.
Acetamide,	v. e. sol.
Propionamide,	v. e. sol.
Oxamide,	sl. sol.
Succinimide,	v. sol.
Asparagine,	m. sol.
Creatine,	m. sol.
Urea,	m. sol.

Urea nitrate,	**v. sol.**
Allylthiourea,	**v. sol.**
Sulphocarbanilide,	**v. sol.**
Uric acid, (G)(insol.)(FK)	**m. sol.**
Guanidine nitrate,	**v. e. sol.**
Theobromine,	**m. sol.**
Alloxantine,	**m. sol.**
Parabanic acid,	**m. sol.**
Dialuric acid,	**m. sol.**
Uramil,	**v. sol.**
Murexide,	**m. sol.**
Alloxan, (G)	**v. sol.**

Hydroxy Acids.

Glycollic acid,	**v. sol.**
Lactic acid,	**v. sol.**
Malic acid,	**sl. sol.**
Tartaric acid,	**sl. sol.**
Citric acid,	**sl. sol.**
Mucic acid,	**m. sol.**
Oxyisobutyric acid,	**v. sol.**

Sugars.

Arabinose,	**m. sol.**
Glucose,	**v. sol.**
Fructose,	**v. sol.**
Galactose,	**m. sol.**
Phenylglucosazone,	**v. sol.**
Sucrose, (G)(FK)	**v. sol.**
Lactose,	**v. sol.**
Maltose,	**v. sol.**
Raffinose,	**v. sol.**

Ethylene Derivatives.

Amylene, (G)	**insol.**
Allyl alcohol,	**miscible**
Allyl isosulphocyanide,	**miscible**
Oleïc acid,	**insol.**
Maleïc acid,	**insol.**
Fumaric acid,	**insol.**
Itaconic acid,	**insol.**
Citraconic acid,	**sl. sol.**
Mesaconic acid,	**sl. sol.**
Aconitic acid,	**m. sol.**
Crotonic acid,	**m. sol.**

Aromatic Hydrocarbons.

Benzene,	**m. sol.**
Toluene,	**sl. sol.**
***o*-Xylene,**	**v. sl. sol.**
***m*- "**	**v. sl. sol.**
***p*- "**	**v. sl. sol.**
Ethylbenzene,	**v. sl. sol.**
Mesitylene, (G)(FK)	**insol.**
Cumene,	**insol.**
Pseudocumene,	**insol.**
Cymene,	**insol.**
Diphenyl,	**v. sl. sol.**
Diphenylmethane,	**insol.**
Triphenylmethane,	**insol.**

Halogen Derivatives.

Chlorbenzene,	**v. sl. sol.**
Brombenzene,	**v. sl. sol.**
Iodbenzene,	**v. sl. sol.**
Hexachlorbenzene,	**v. sl. sol.**
Dibrombenzene,	**v. sl. sol.**
***p*-Chlortoluene,**	**v. sl. sol.**

Nitro Derivatives.

Nitrobenzene,	**v. sol.**
Dinitrobenzene,	**m. sol.**
***o*-Nitrotoluene,**	**m. sol.**
***p*- "**	**v. sl. sol.**
1-2-4-Dinitrotoluene,	**sl. sol.**
Trinitrotoluene,	**m. sol.**
***m*-Nitrochlorbenzene,**	**sl. sol.**
***p*- "**	**sl. sol.**
***m*-Nitro-*p*-chlortoluene,**	**m. sol.**

Amido Derivatives.

Aniline,	**miscible**
***o*-Toluidine,**	**miscible**
***p*- "**	**v. sol.**
Xylidine, asym. *m*,	**sl. sol.**
Dimethylaniline,	**v. sl. sol.**
Diethylaniline,	**v. sl. sol.**
Methyldiphenylamine,	**sl. sol.**
***m*-Nitraniline,**	**v. sol.**
***p*- "**	**v. sol.**

Phenols.

Phenol,	**v. sol.**
***o*-Cresol,**	**miscible**
***m*- "**	**miscible**
***p*- "**	**miscible**
Pyrocatechin,	**v. e. sol.**
Resorcin,	**v. e. sol.**
Hydroquinone,	**v. sol.**
Pyrogallol,	**v. e. sol.**
Orcin,	**v. sol.**
Guaiacol,	**miscible**
Anisol,	**miscible**
Phenetol,	**miscible**
Thymol,	**v. sol.**
Menthol,	**m. sol.**

Substituted Phenols.

***o*-Nitrophenol,**	**v. e. sol.**
***p*- "**	**v. sol.**
1-2-4-Dinitrophenol,	**v. sol.**
Trinitrophenol,	**v. sol.**
***p*-Nitroanisol,**	**sl. sol.**
Eugenol,	**m. sol.**
Anethol,	**sl. sol.**
***o*-Amidophenol,**	**v. sol.**
***p*- "**	**v. sol.**

Alcohols.

Benzyl alcohol,	**miscible**

Cinnamic alcohol,	miscible

Ethers.

Benzylethyl ether,	sl. sol.

Aldehydes.

Benzaldehyde,	v. sol.
Anisaldehyde,	miscible
m-Nitrobenzaldehyde,	v. e. sol.
Cinnamic aldehyde,	miscible
Vaniline,	v. sol.
Heliotropine,	v. sol.

Monobasic Acid.

Benzoic acid,	v. sol.
Benzoic anhydride,	v. sol.
α-Toluic acid,	v. sol.
o- " "	v. sol.
m- " "	v. sol.
p- " "	m. sol.
Cinnamic acid,	m. sol.

Substitution-Products.

m-Brombenzoic acid,	v. e. sol.
o-Nitrobenzoic acid,	m. sol.
m- " "	m. sol.
p- " "	sl. sol.
o-Amidobenzoic acid,	v. sol.
m- " "	v. sol.
p- " "	v. sol.
o-Hydroxybenzoic acid,	v. e. sol.
m- " "	v. sol.
p- " "	v. sl. sol.
o-Nitrocinnamic acid,	v. sol.
Nitrophenylpropiolic acid,	m. sol.
Gallic acid,	m. sol.
Anisic acid,	m. sol.
Coumarin,	m. sol.

Dibasic Acids.

o-Phthalic acid,	v. sl. sol.
p- " "	v. sl. sol.
Phthalimide,	v. e. sol.

Ethereal Salts.

Methyl benzoate,	miscible
Ethyl benzoate,	v. e. sol.
Isobutyl benzoate,	insol.
Amyl benzoate,	insol.
Methyl salicylate,	m. sol.
Phenyl cyanide,	miscible
Benzyl cyanide,	miscible
p-Cyantoluene,	v. sol.
Phenyl acetate,	miscible
Phenyl salicylate,	sl. sol.
Phenyl isosulphocyanate,	m. sol.
Ethylphenyl carbamate,	v. e. sol.

Sulphonic Acids.

Benzenesulphon chlorid,	action
o-Amidobenzenesulphonic acid,	v. e. sol.
m-Amidobenzenesulphonic acid,	v. sol.
p-Amidobenzenesulphonic acid,	v. e. sol.
Benzoicsulphinide (saccharin),	m. sol.

Acid Amides and Anilides.

Formanilide,	v. sol.
Acetanilide,	v. sol.
Benzamide,	v. sol.
Benzanilide,	sl. sol.
Hippuric acid,	v. sol.
p-Acettoluide,	sl. sol.
Benzenesulphonamide,	v. e. sol.
Carbazol,	m. sol.

Naphthalene and Derivatives.

Naphthalene, (G)(FK)	v. sl. sol.
α-Naphthol,	m. sol.
β- "	sl. sol.
α-Naphthylamine,	v. sol.
β- "	m. sol.
Nitroso-β-naphthol,	m. sol.
Acetnaphthalide,	sl. sol.

Pyridine and Quinoline.

Pyridine,	miscible
Picoline,	miscible
Collidine,	miscible
Nicotine,	m. sol.
Dihydrocollidinedicarbonic-acid diethylester,	sl. sol.
Quinoline,	miscible
Isoquinoline,	sl. sol.

Terpenes.

Terebene,	insol.
Carvol,	sl. sol.
Carvene,	sl. sol.
Pinene,	insol.
Sylvestrene,	insol.
Terebenthene,	insol.
Borneol camphor,	m. sol.
Camphoric acid,	insol.

Unclassified.

Iodosobenzene,	sl. sol.
Iodoxybenzene,	m. sol.
Diphenyliodonium iodide,	sl. sol.
Diphenyliodonium chromate,	insol.
Acetophenone,	m. sol.
Quinone,	m. sol.
Chloranil,	m. sol.
Benzil,	m. sol.
Benzoin,	insol.
β-Benzyldioxime,	v. e. sol.
Haematoxylin,	m. sol.
Haemaglobin,	sl. sol.

Cholesterine,	insol.
Amygdaline,	v. sol.
Codea nitrate,	insol.
Cocaine,	insol.
Cocaine hydrochloride,	m. sol.
Cubebina,	v. sol.
Digitaline,	v. e. sol.
Phloridzine,	v. e. sol.
Picrotoxine,	v. e. sol.
Piperidine,	sl. sol.
Piperine,	insol.
Salicine,	v. sol.
Santonine,	insol.
Strychnine,	insol.
" acetate,	insol.
" bromide,	insol.
" chloride,	insol.
Anthracene,(G)(FK)	insol.
Phenanthrene,	insol.
Anthraquinone,	insol.
Alizarine,	m. sol.
Brucia,	m. sol.
Cinchonidia,	sl. sol.
Cinchona,	insol.
Codeia,	m. sol.
Cubebine,	m. sol.
Meconine,	insol,
Morphia,	insol.
Narcotine,	insol.
Quinine,	insol.
" hypophosphite,	m. sol.
Quinine iodide,	insol.
Quinine sulphate, (G)(FK)	insol.
Quinidia,	insol.
Theine,	sl. sol.
Tannic acid,	sl. sol.
Indigo, (G)	sl. sol.
Gutta percha, (G)	action
Starch, (G) "swells up and mixes as in water."	
Isinglass, (G)	"semifluid."
Camphor, (G)	v. sol.
Gum copal (G)	v. sl. sol.
Gun cotton,(G)	sl. sol.
Bengal silk, (G)	insol.

Experiments at Higher Temperatures.

The statements of Gore[1] to the effect that sulphur and phosphorus are soluble in ammonia have led us to study the action of ammonia on these and some other substances at temperatures considerably above the boiling-point of the solvent at atmospheric pressure. In making the tests a glass tube sufficiently strong to withstand the pressure was placed in a bath of liquid ammonia and then charged with a small quantity of the substance to be tested, together with 2 or 3 cc. of liquid ammonia. The tube was sealed before the blowpipe, after which it was removed from the refrigerating-bath and allowed to warm up to the temperature of the laboratory. It was found that a number of substances, which at —38° were not perceptibly soluble, dissolved abundantly at 25°.

Results.

Sulphur.—Sulphur dissolves slowly, forming a dirty green colored solution, which on refrigeration changes to a red color, without, however, the separation of any solid from the solution. The solution is a conductor of electricity. On evaporation a red liquid is left behind which mixes with water with the separation of sulphur.

[1] *Loc. cit.*

Selenium.—Selenium dissolves very slowly, forming a solution which resembles the sulphur solution.

Phosphorus.—Phosphorus is acted upon by ammonia at 25°, but much more slowly than is sulphur. It forms a dark brown, almost opaque, solution which deposits no solid on being subjected to refrigeration. The solution is a conductor of electricity.

Hexane.—Hexane is very slightly soluble in ammonia at 25°. On cooling the solution becomes milky.

Benzene.—Benzene, which is but moderately soluble at —38°, is extremely soluble at 25°. On cooling the solution a solid, presumably benzene, crystallizes out.

Metaxylene.—Xylene is but very slightly soluble at —38°. At the higher temperature it is miscible in all proportions. On cooling the solution, the xylene separates abundantly.

Triphenylmethane.—This compound, which is not perceptibly soluble at —38°, is readily soluble at the higher temperature. The hydrocarbon crystallizes out when the solution is cooled.

Naphthalene.—Evaporation of a portion of solvent which, at atmospheric pressure, had been in contact with powdered naphthalene, showed the substance to be very slightly soluble. It dissolves abundantly when the solvent is warmed, separating again when the solution is cooled.

Anthracene.—Anthracene is but very slightly soluble at 25°.

Pinene.—Pinene dissolves slightly at 25°. When cooled, the solution becomes milky in consequence of separation of the solute.

Chlorbenzene and Iodobenzene.—These two halogen products, which are but very slightly soluble in ammonia at —38°, are miscible in all proportions at the higher temperature.

Dibrombenzene.—Dibrombenzene dissolves very easily at 25°. When the solution is cooled the substance separates out rapidly in beautifully formed crystals.

Phthalic Acid.—The phthalic acid crystals are disintegrated, forming, probably, ammonium phthalate, which is insoluble in ammonia even at a temperature of 25°.

Benzanilide.—Benzanilide is more soluble at 25° than it is at —38°.

Stearic Acid.—Stearic acid is very slightly soluble at 25°. On cooling the solution a slight separation of solid takes place.

Succinic Acid.—The crystals of the acid are disintegrated by the ammonia forming presumably ammonium succinate, which, however, remains undissolved at 25°.

Parahydroxybenzoic Acid.—This acid, which is but slightly soluble at —38°, dissolves abundantly at 25°. It separates slowly when the solution is cooled.

Cadmium Iodide.—Cadmium iodide is not perceptibly more soluble at the higher temperature than at —38°.

Ammonium Chromate.—This salt is somewhat more soluble at the higher temperature. On cooling the solution, yellow crystals separate on the walls of the tube.

Potassium Chromate.—Potassium chromate is insoluble at the higher as well as the lower temperature.

UNIVERSITY OF KANSAS,
LAWRENCE, June, 1898.

DETERMINATION OF THE MOLECULAR RISE IN THE BOILING-POINT OF LIQUID AMMONIA.

BY E. C. FRANKLIN AND C. A. KRAUS.

In view of the position occupied by liquid ammonia as a solvent, determinations of the molecular elevation of its boiling-point produced by substances in solution, become a matter of interest. For the purpose of measuring the constant experimentally, a modified form of Beckmann's boiling-point apparatus, was devised and used with fairly satisfactory results. The difficulties inherent in the boiling-point method certainly persist when the solvent used boils 60° below the laboratory temperature, and, in further consideration of the surprisingly small effect of a dissolved solute on the boiling-point of the solvent, we consider the measurements made to be fairly satisfactory.

Apparatus.

Fortunately for our purpose, the boiling-point of ammonia at atmospheric pressure lies above the freezing-point of mercury.

It was consequently found to be a comparatively simple matter to adapt the Beckmann method to the determination of the boiling-point elevation of ammonia solutions. After several attempts with various modifications of the apparatus, the form described in the following was finally devised and used in making the determinations given in this paper:

For the boiling-vessel a vacuum-jacketed Dewar tube was used. This is represented one-half the natural size by Fig. 1. The vessel has a capacity of 25 to 30 cc. when filled to a point half way between the top of the platinum cylinder and the cork stopper. AA are heavy platinum wires sealed in with red lead glass. B is a coil of small platinum wire connecting the interior ends of the two heavy wires, the joints being secured by means of gold solder. C is the filling-material consisting, in these experiments, of a layer of garnets sufficient to protect the coil B, covered with a layer of the platinum tetrahedra of Beckmann.[1] D is a platinum cylinder covering the bulb of the thermometer, and introduced for the purpose of protecting the thermometer from the effects of radiation.[2] E is an ordinary Beckmann thermometer made by F. O.

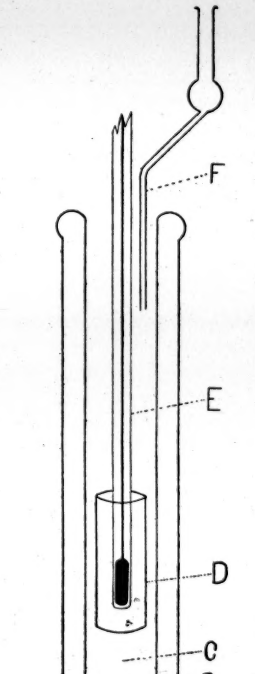


Fig. 1.

[1] Ztschr. physikal. Chem., **21**, 284.
[2] Jones: This JOURNAL, **19**, 582.

R. Götze, in Leipsic, for determinations by the boiling-point method. It is held in place by a perforated cork stopper provided with a small tube, F, for the escape of the ammonia vapor. In some experiments a drying-tube containing soda-lime was attached to F. It was not considered feasible to condense the ammonia vapor and to return it to the boiling-tube as is done with ordinary solvents. It was consequently decided to allow the vapors to escape, and to determine the amount of solvent present after each boiling-point measurement, by weighing the whole piece of apparatus with its contents. For this purpose a balance was placed on a stable frame above the working table, a hole was cut through the bottom of the balance-case, and the boiling-tube with the thermometer in place was suspended by means of a wire from the arm of the balance. A battery, rheostat, and ammeter are conveniently placed for the purposes respectively of furnishing, regulating, and measuring the current used in boiling the liquid in the boiling-tube.

The considerably greater quantity of mercury contained in the bulb of the thermometer when used in measuring temperatures as low as the boiling-point of ammonia would have the effect of giving scale readings on a thermometer made to be used at much higher temperatures, greater than the true differences in temperature. Measurements made by Grützmacher[1] give as a result, that between the temperatures of —35° and —30° with the mercury column at the same temperature, the value of one scale division on the thermometer is equal to 0.982°; with the mercury column at 0° and the bulb at —35° to —30°, one scale division was found to be equal to 0.977°. In our experiments the temperature of a portion of the mercury column was about 17° to 22°, which would further slightly diminish the value of a scale division to about 0.975°. However, this correction has not been introduced into the tables accompanying this paper.

Although the liquid boils gently as the effect of heat conducted and radiated to the interior of the tube, the ammonia remains considerably superheated, as a few attempts to get

[1] Grützmacher: Ztschr. für Instrumentenkunde, 1896, 202; and E. Beckmann: Ztschr. physikal. Chem., 21, 253.

concordant measurements of boiling-point elevations soon convinced us. More vigorous boiling was brought about by passing a current of electricity through the wire ABA. The temperature falls with increasing current more and more slowly, until an expenditure of about 20 watts was reached. Currents above this strength produced no further depression of the thermometer.

When the attempt was made to determine accurately the boiling-point of the solvent, it was found that the mercury fell continuously in the capillary of the thermometer as the solvent boiled away. The depression of the mercury was slow, but was distinctly measurable. In order to make corrections for this effect, a scale was affixed to the tube on which was marked the contents in grams, from the lowest point at which measurements were made to the highest; from 10 to 20 grams. It was found as the mean of several experiments that the difference between the apparent boiling-points when the tube was charged with 10 and 20 grams of solvent respectively, was 0.042°, giving a correction of 0.004° to be added to successive measurements differing from each other by one scale division.

The cause of this behavior is undoubtedly to be found in the diminishing weight of the supernatant liquid as the solvent boils away. Further than this, there is the factor of the varying specific gravity of the solution which must affect the correction to be made, and this effect, in the case of concentrated solutions, may not be inconsiderable. No attempts at corrections for variations from this latter cause have, however, been made.

Making the Determinations.

The boiling-tube, tared with the thermometer, garnets, and platinum cylinder, was charged with solvent from the stock cylinder as follows: In Fig. 2, *L* is the stock cylinder, *M* is the discharging valve, *N* is the boiling-tube, and *O* is a bottle containing water. On opening the valve *M*, a portion of the ammonia in the form of gas passes through *N* into *O*, and is there absorbed and saved, while the liquid collects in the tube *N*. After collecting from 16 to 18 grams of solvent in

the boiling-tube it is removed to its position under the balance-case, the thermometer is introduced, and the whole left at rest until the thermometer has cooled down to the temperature of the slowly boiling liquid. The current which is then

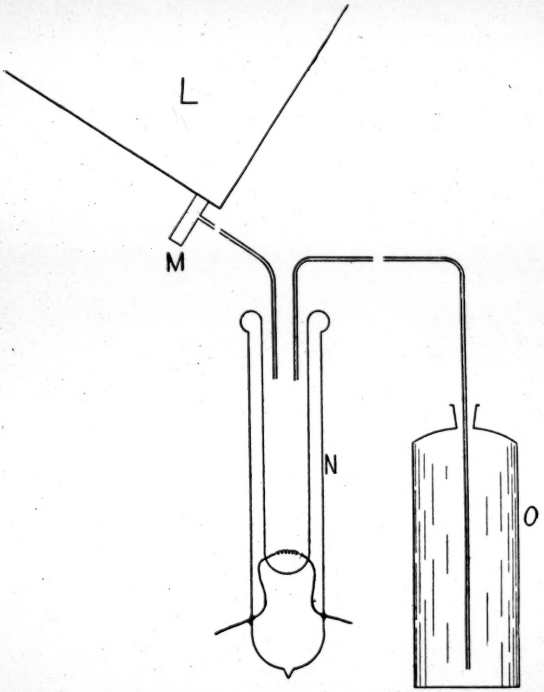


Fig. 2.

turned on, causes a vigorous boiling of the solvent and a rapid decline of the temperature. As soon as the mercury has become stationary and is not further affected by gentle rapping of the brass cap of the thermometer, the temperature is read, and immediately thereafter the current is stopped, and the

scale on the boiling-tube noted. The cork bearing the thermometer is then removed sufficiently to permit the introduction of the solute, which is accomplished in the case of liquids by means of Beckmann's pipette, in the case of those solids which permit it, in the form of compressed tablets, while other solids are introduced by weighing crystal fragments from specimen tubes. These weights are given in the tables below under "Gm. Solute." The thermometer is then replaced in position, and the operation of determining the boiling-point is again carried out as described above, the proper correction being made for the solvent boiled away. As soon as this is accomplished, the boiling-tube is loosened from its fastenings and weighed. The weight of the solute, plus the weight of the empty apparatus, subtracted from the weight thus obtained, gives the weight of the solvent. These values are given in the tables under "Gm. Solvent." The experiment as above described is repeated until a sufficient number of determinations have been made. The values under "Constant" are calculated by means of the formula,

$$\frac{\text{Gm. solvent} \times \text{elevation} \times \text{mol. wt.}}{\text{Gm. solute} \times 100}$$

The remaining columns need no explanation.

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
		1. Water.			
16.05	0.1469	0.92	5.00	0.174	3.42
15.17	0.1992	1.31	7.28	0.256	3.51
14.32	0.2626	1.83	10.17	0.356	3.50
13.58	0.3745	2.76	15.33	0.529	3.45
12.85	0.4106	3.20	17.78	0.613	3.45
11.91	0.5528	4.64	25.78	0.886	3.44
11.22	0.5911	5.27	29.27	1.009	3.45
10.36	0.8431	8.14	45.22	1.554	3.44
9.87	0.8431	8.54	47.44	1.631	3.44
9.13	1.1014	12.06	67.03	2.308	3.45
8.27	1.6261	19.66	109.22	3.852	3.53

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{10}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
		2. Water.			
15.96	0.2399	1.51	8.39	0.254	3.04
14.65	0.4006	2.74	15.22	0.497	3.27
13.28	0.5346	4.03	22.39	0.736	3.29
11.93	0.7792	6.53	36.28	1.210	3.33
10.96	0.9342	8.52	47.32	1.604	3.39
10.00	1.0542	10.53	58.55	1.987	3.39
9.07	1.0542	11.63	64.55	2.199	3.42
19.79	1.0542	5.33	29.61	1.011	3.42
18.47	1.0542	5.71	31.72	1.078	3.40
16.97	1.0542	6.21	34.50	1.116	3.38
15.60	1.0542	6.76	37.55	1.272	3.39
14.07	1.0542	7.49	41.61	1.409	3.39
11.78	1.0542	8.95	49.72	1.663	3.29
10.84	1.3149	12.13	67.39	2.300	3.42
9.92	1.6473	16.60	92.22	3.447	3.74
8.71	1.6473	18.91	105.05	3.966	3.78
		3. Ethyl Alcohol.			
16.84	0.0642	0.38	0.83	0.019	2.24
15.98	0.2550	1.60	3.47	0.108	3.11
15.23	0.3534	2.31	5.02	0.161	3.20
14.54	0.4584	3.15	6.83	0.230	3.36
13.83	0.6155	4.45	9.67	0.321	3.32
13.04	0.8328	6.39	13.90	0.463	3.34
12.33	1.0876	8.82	19.17	0.645	3.36
11.80	1.2002	10.17	22.11	0.800	3.62
11.12	1.3772	12.38	26.91	0.905	3.36
10.51	1.5365	14.63	31.80	1.071	3.37
9.97	1.6212	16.26	35.22	1.189	3.37
9.50	1.7750	18.68	40.61	1.384	3.41
8.96	1.9660	21.94	47.70	1.611	3.38
8.48	2.2680	26.74	58.13	1.961	3.38
7.99	2.5372	31.75	69.02	2.317	3.36
7.52	2.9004	38.56	83.83	2.827	3.38
6.73	3.0170	44.83	97.46	3.202	3.29
		4. Propyl Alcohol.			
14.13	0.0702	0.49	0.81	0.028	3.38
13.26	0.2420	1.83	3.05	0.106	3.49
11.79	0.5585	4.74	7.90	0.261	3.31
10.65	0.7182	6.74	11.23	0.371	3.30

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
9.70	0.9514	9.81	16.35	0.527	3.22
8.35	0.9514	11.39	18.95	0.612	3.22
18.52	0.9514	5.14	8.57	0.294	3.43
15.95	0.9514	5.83	9.72	0.329	3.31
14.89	1.1875	7.98	13.30	0.436	3.28
13.77	1.4332	10.41	17.35	0.565	3.26
12.37	1.7305	14.00	23.33	0.744	3.19
11.37	2.0319	17.87	29.78	0.919	3.09
10.57	2.3310	22.05	35.92	1.107	3.01
9.79	2.6872	27.45	45.75	1.346	2.94
8.87	3.0765	34.69	57.82	1.649	2.85
8.07	3.0765	38.13	66.55	1.797	2.83
7.46	3.5355	47.40	79.00	2.222	2.81
6.96	3.5355	50.81	84.68	2.378	2.81
6.31	3.5355	56.04	93.40	2.572	2.75
		5. Phenol.			
15.94	0.1141	0.74	0.79	0.028	3.68
13.91	0.3326	2.39	2.54	0.086	3.38
12.53	0.7951	6.31	6.71	0.200	2.98
11.68	1.2791	11.37	12.10	0.373	3.08
10.08	1.5957	15.83	16.84	0.509	3.02
9.20	1.5957	17.35	18.46	0.547	2.97
16.15	1.5957	9.88	10.51	0.334	3.18
14.29	1.5957	11.17	11.88	0.363	3.05
13.31	1.9102	14.35	15.26	0.480	3.14
12.14	1.9102	15.73	16.73	0.512	3.06
11.30	2.4448	21.64	23.02	0.715	3.10
8.68	2.4448	28.17	29.97	0.820	2.73
7.86	2.4448	31.11	33.10	0.914	2.76
		6. Pyrocatechin.			
15.51	0.1142	0.74	0.67	0.012	1.79
13.76	0.2605	1.89	1.72	0.045	2.67
12.65	0.5652	4.47	4.06	0.132	3.25
11.77	0.7811	6.64	6.04	0.198	3.28
10.69	1.0299	9.64	8.76	0.280	3.20
8.97	1.0299	11.48	10.44	0.344	3.30
18.59	1.0299	5.54	5.04	0.168	3.34
14.09	1.0299	7.31	6.65	0.210	3.16
12.87	1.3759	10.69	9.72	0.314	3.23
12.17	1.3759	11.31	10.28	0.328	3.19

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{100}{wt.}$ gm. mol. solute in 100 gr. solvent.	Elevation.	Constant.
11.19	2.0084	17.94	16.31	0.524	3.21
10.41	2.4862	23.88	21.71	0.690	3.18
9.16	2.4862	27.14	24.67	0.768	3.11
		7. Resorcin.			
17.32	0.1757	1.02	0.93	0.032	3.47
16.34	0.4592	2.81	2.55	0.085	3.33
14.69	0.4592	3.13	2.85	0.103	3.62
13.62	0.8265	6.07	5.50	0.194	3.52
12.77	0.8265	6.47	5.88	0.212	3.60
11.25	1.1547	10.26	9.33	0.327	3.59
10.15	1.1547	11.38	10.35	0.370	3.58
9.43	1.4687	15.58	14.16	0.497	3.51
8.63	1.4687	17.02	15.47	0.541	3.50
7.23	1.4687	20.32	18.47	0.645	3.49
		8. Hydroquinone.			
17.95	0.1002	0.56	0.51	0.024	4.73
16.45	0.2682	1.63	1.48	0.056	3.78
14.97	0.5314	3.55	3.24	0.122	3.78
13.77	0.6517	4.73	4.30	0.162	3.77
12.81	0.8306	6.48	5.89	0.224	3.80
11.76	1.0401	8.84	8.04	0.307	3.82
10.67	1.2402	11.62	10.56	0.403	3.81
9.91	1.4113	14.24	12.96	0.497	3.82
9.09	1.4113	15.52	14.11	0.543	3.85
17.64	1.4113	8.00	7.27	0.304	4.18
16.29	1.4113	8.66	7.86	0.328	4.17
14.31	1.4113	9.86	8.96	0.366	4.08
13.46	1.8166	13.50	12.27	0.492	4.01
12.00	1.8166	14.45	13.14	0.558	4.27
10.70	1.8166	16.98	15.44	0.630	4 08
9.28	1.8166	19.58	17.80	0.720	4.04
8.08	1.8166	22.49	20.45	0.839	4.10
		9. Hydroquinone.			
13.44	0.1052	0.78	0.71	0.019	2.81
12.57	0.2369	1.88	1.71	0.061	3.57
11.33	0.6657	5.88	5.33	0.189	3.50
10.27	1.2243	11.92	10.83	0.398	3.67
8.78	1.2243	13.94	12.67	0.446	3.52
17.93	1.2243	6.83	6.21	0.220	3.54
15.95	1.2243	7.67	6.97	0.262	3.76

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
13.78	1.2243	8.88	8.07	0.311	3.85
11.84	1.2243	10.34	9.40	0.352	3.75
10.00	1.2243	12.20	11.10	0.420	3.77
8.52	1.7780	20.87	18.97	0.719	3.79
		10. Sugar.			
15.61	0.0693	0.46	0.13	0.007	5.39
14.82	0.2548	1.72	0.53	0.019	3.18
13.99	0.6481	4.63	1.36	0.047	3.25
13.03	1.0547	8.10	2.37	0.080	3.25
11.82	1.5069	12.75	3.73	0.126	3.30
11.06	1.6089	14.55	4.25	0.148	3.41
10.30	2.3095	22.43	6.56	0.237	3.57
9.64	2.6523	27.51	8.04	0.301	3.71
8.76	3.3905	38.71	11.32	0.448	3.93
7.74	4.6151	59.64	17.44	0.761	4.35
6.89	4.6151	66.99	19.60	0.885	4.52
6.09	4.6151	75.79	22.16	1.042	4.70
		11. Sugar.			
17.35	0.0480	0.28	0.08	0.000	0.00
15.83	0.7382	4.66	1.37	0.039	2.90
14.44	1.4308	9.91	2.90	0.113	3.90
13.31	2.1426	16.10	4.71	0.180	3.82
11.95	2.8771	24.07	7.04	0.271	3.85
11.13	3.2691	30.05	8.79	0.330	3.85
9.90	3.8325	38.72	11.32	0.467	4.12
8.97	3.8325	42.73	12.49	0.527	4.22
18.51	3.8325	20.71	6.06	0.228	3.77
16.52	3.8325	23.20	6.78	0.263	3.88
14.37	3.8325	26.67	7.80	0.303	3.89
12.67	3.8325	30.25	8.84	0.357	4.04
11.18	3.8325	34.28	10.02	0.425	4.24
9.58	3.8325	40.01	11.70	0.502	4.29
8.25	3.8325	46.46	13.58	0.600	4.42
7.47	3.8325	51.17	14.96	0.676	4.52
		12. Urea.			
16.54	0.0284	0.17	0.29	0.015	5.24
15.77	0.1339	0.85	1.42	0.054	3.82
15.11	0.2850	1.89	3.15	0.100	3.18
14.49	0.5154	3.56	5.93	0.189	3.19

Gm. solvent.	Gm. solute	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
13.78	0.7263	5.27	8.78	0.274	3.12
13.07	1.0375	7.95	13.25	0.408	3.08
12.36	1.2086	9.78	16.30	0.486	2.98
11.69	1.4906	12.75	21.25	0.615	2.89
11.16	1.5678	14.05	23.42	0.663	2.83
10.51	1.8193	17.31	28.85	0.782	2.71
9.96	2.1244	21.32	35.53	0.904	2.54
9.94	2.3724	26.53	44.22	0.997	2.26
		13. Urea.			
13.94	0.4120	2.98	4.97	0.167	3.37
13.35	0.4120	3.09	5.15	0.177	3.44
12.63	0.7438	5.89	9.82	0.313	3.19
11.99	1.0157	8.46	14.10	0.433	3.07
11.33	1.0157	8.97	14.95	0.452	3.02
10.38	1.0157	9.79	16.32	0.484	2.97
9.75	1.0157	10.42	17.37	0.520	2.99
8.43	1.0157	12.05	20.08	0.587	2.92
7.29	1.0157	13.93	23.22	0.669	2.88
6.78	1.0157	14.95	24.92	0.714	2.86
6.19	1.0157	16.41	27.35	0.760	2.78
5.43	1.0157	18.70	31.17	0.854	2.74
		14. Pyridine.			
17.64	0.2138	1.21	1.53	0.050	3.26
16.49	0.2138	1.30	1.64	0.049	2.39
15.20	0.5994	3.94	5.00	0.164	3.28
14.10	0.5994	4.25	5.38	0.171	3.18
12.97	1.0844	8.36	10.58	0.321	3.03
12.22	1.0844	8.75	11.07	0.342	3.04
11.30	1.6004	14.16	17.92	0.513	2.86
10.59	1.9576	18.48	23.39	0.646	2.82
9.81	2.4151	24.62	31.16	0.818	2.60
9.06	2.9046	32.06	40.58	1.004	2.47
8.29	3.3648	40.58	51.50	1.211	2.36
7.60	3.8971	51.28	64.66	1.423	2.19
6.92	4.4814	64.76	80.97	1.681	2.05
6.14	5.2166	85.08	107.70	2.031	1.88
5.29	5.2166	98.74	124.93	2.240	1.79
		15. Aniline.			
17.90	0.2928	1.64	1.55	0.069	3.92
16.94	0.5370	3.17	3.41	0.123	3.61
15.96	0.7428	4.65	5.00	0.169	3.38

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	1/10 gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
14.66	0.7428	5.07	5.45	0.185	3.40
13.73	1.0727	7.82	8.41	0.286	3.40
12.80	1.3046	10.15	10.91	0.365	3.34
11.99	1.6146	13.47	14.49	0.475	3.28
11.04	2.0144	18.24	19.61	0.634	3.23
10.10	2.6763	26.50	28.50	0.904	3.18
9.16	2.9880	32.62	35.08	1.095	3.12
		16. Ortho-nitrophenol.			
13.65	0.1026	0.75	0.54	0.027	4.99
12.72	0.3624	3.09	2.22	0.076	3.43
11.93	0.7670	6.43	4.62	0.157	3.39
11.15	1.2079	10.83	7.78	0.263	3.38
10.08	2.1302	21.13	15.20	0.499	3.28
		17. Acetic Acid.			
15.60	0.0328	0.21	0.35	0.013	3.77
13.62	0.2717	1.99	3.32	0.073	2.18
11.90	0.6902	5.80	9.67	0.187	1.90
10.00	1.2504	12.50	20.83	0.334	1.55
19.15	1.2504	6.53	10.88	0.223	2.01
17.25	1.2504	7.25	12.08	0.239	1.94
13.29	1.2504	9.41	15.67	0.297	1.85
10.59	1.2504	11.80	19.67	0.346	1.70
9.15	1.2504	13.66	22.77	0.395	1.67
8.12	1.2504	15.40	25.67	0.424	1.58
		18. Sodium Acetate.			
16.26	0.0441	0.27	0.38	0.014	3.71
15.04	0.0799	0.53	0.74	0.025	3.40
13.65	0.1930	1.41	1.96	0.060	3.10
10.51	0.3447	3.28	4.56	0.092	2.15
		19. Benzene.			
17.09	0.2690	1.57	2.01	0.064	3.17
15.62	0.5675	3.63	4.66	0.133	2.86
14.35	0.7150	4.98	6.38	0.164	2.57
13.11	0.7941	6.04	7.74	0.195	2.51
11.82	0.7941	6.70	8.60	0.213	2.47
10.84	0.7941	7.30	9.36	0.237	2.52
9.36	0.7941	8.28	10.61	0.263	2.47
8.53	0.7941	9.28	11.90	0.297	2.49
7.66	0.7941	10.33	13.24	0.321	2.42

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
15.91	0.7941	4.97	6.37	0.179	2.80
13.31	0.7941	5.95	7.63	0.199	2.60
11.76	0.7941	6.73	8.63	0.223	2.58
10.37	0.7941	7.63	9.77	0.242	2.47
9.41	0.7941	8.41	10.78	0.266	2.46
8.32	0.7941	9.51	12.19	0.300	2.45
7.76	0.7941	10.20	13.07	0.317	2.42
		20. Benzene.			
17.01	0.2386	1.40	1.79	0.038	2.21
15.56	0.5390	3.55	4.55	0.113	2.54
14.49	0.7422	5.24	6.72	0.176	2.68
13.50	0.8850	6.56	8.41	0.225	2.68
11.97	0.8850	7.39	9.47	0.238	2.51
10.46	0.8850	8.46	10.84	0.262	2.41
9.03	0.8850	9.80	12.56	0.283	2.25
7.04	0.8850	12.57	16.11	0.319	1.96
17.76	0.8850	4.98	6.38	0.134	2.10
16.46	0.8850	5.38	6.89	0.156	2.26
14.91	0.8850	5.94	7.61	0.166	2.17
13.22	0.8850	6.69	8.59	0.189	2.20
10.81	0.8850	8.19	10.50	0.220	2.08
9.54	0.8850	9.28	11.90	0.254	2.12
8.68	0.8850	10.20	13.07	0.277	2.11
		21. Potassium Iodide.			
13.37	1.0673	7.98	4.81	0.178	3.70
12.55	2.3096	18.40	11.08	0.491	4.23
11.37	4.9438	43.48	26.19	1.351	5.16
		22. Potassium Iodide.			
14.39	0.3113	2.16	1.30	0.038	2.92
13.08	0.8686	6.64	4.00	0.155	3.89
12.47	1.6945	13.59	8.19	0.315	3.85
11.81	3.1831	26.95	16.23	0.720	4.34
		23. Potassium Iodide.			
17.39	0.2934	1.60	1.04	0.016	1.59
16.08	0.9186	5.71	3.44	0.109	3.20
14.90	1.6414	11.01	6.64	0.248	3.78
13.75	1.8312	13.32	8.02	0.306	3.87

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{10}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
12.64	2.1414	16.94	10.20	0.408	4.05
11.99	2.1414	17.86	10.76	0.433	4.08
11.07	2.1414	19.34	11.65	0.471	4.09
10.44	2.1414	20.51	12.35	0.507	4.15
8.49	2.1414	25.22	15.80	0.650	4.33
18.87	2.1414	11.34	6.83	0.255	3.41
16.06	2.1414	13.34	8.04	0.306	3.85
14.43	2.1414	14.84	8.94	0.346	3.92
12.69	2.1414	16.87	10.16	0.412	4.10
12.04	2.1414	17.79	10.71	0.441	4.17
10.85	2.1414	19.74	11.90	0.480	4.09
10.31	2.1414	20.77	12.51	0.526	4.26
9.36	3.5356	37.77	22.75	1.129	5.02
8.52	4.4406	52.12	31.40	1.678	5.41
7.87	4.4406	56.43	34.00	1.994	5.94

24. Sodium Nitrate.

17.73	0.2744	1.53	1.80	0.043	2.37
16.63	0.2744	1.65	1.94	0.054	2.78
14.24	0.6066	4.26	5.01	0.150	2.99
12.94	1.2554	9.70	11.41	0.384	3.37
11.29	1.2554	11.12	13.08	0.457	3.49
10.41	1.7373	16.69	19.63	0.731	3.72
9.24	2.3107	25.01	29.42	1.190	4.04
8.30	2.7494	33.11	38.95	1.782	4.58
7.80	2.7494	35.24	41.46	1.997	4.82
6.65	2.7494	41.33	48.62	2.547	5.24

25. Ammonium Nitrate.

15.51	0.2924	1.88	2.35	0.087	3.69
14.46	0.2924	2.02	2.52	0.101	4.00
13.31	0.4920	3.70	4.62	0.166	3.59
12.38	0.7228	5.84	7.30	0.263	3.60
11.62	0.9776	8.41	10.51	0.388	3.69
10.73	1.2694	11.83	14.80	0.557	3.77
10.00	1.6499	16.50	20.62	0.834	4.03
9.42	2.0304	21.55	26.74	1.192	4.43
8.47	2.0304	23.96	29.94	1.368	4.57
7.32	2.0304	27.73	34.66	1.675	4.83
6.32	2.0304	32.12	40.15	2.100	5.23

Gm. solvent.	Gm. solute.	Gm. solute per 100 g. solvent.	$\frac{1}{100}$ gm. mol. wt. solute in 100 gr. solvent.	Elevation.	Constant.
		26. Metallic Sodium.			
10.20	0.1133	1.11	4.83	0.104	2.13
9.26	0.2145	2.31	10.04	0.207	2.07
8.43	0.3312	3.92	17.04	0.306	1.79
6.47	0.3312	5.10	22.17	0.317	1.43
		27. Metallic Sodium.			
14.10	0.1189	0.84	3.65	0.074	2.04
12.52	0.1189	0.95	4.13	0.090	2.18
10.82	0.1189	1.10	4.78	0.117	2.45
9.65	0.1189	1.22	5.30	0.134	2.53
8.51	0.1189	1.40	6.08	0.146	2.40
7.63	0.1189	1.56	6.78	0.159	2.35
		28. Metallic Sodium.			
16.87	0.6081	3.60	15.65	0.281	1.80
15.71	0.6081	3.87	16.83	0.296	1.76
14.09	0.6081	4.32	18.78	0.321	1.71
12.64	0.6081	4.81	20.92	0.335	1.60
11.04	0.6081	5.51	22.39	0.355	1.48
		29. Metallic Lithium.			
15.79	0.0580	0.36	5.14	0.040	0.76
13.76	0.1569	1.14	16.30	0.272	1.67
12.89	0.1569	1.22	17.43	0.293	1.69
10.18	0.1569	1.54	22.00	0.317	1.44
9.11	0.1569	1.72	24.60	0.335	1.36
8.25	0.1569	1.90	27.14	0.358	1.31
7.64	0.1569	2.05	29.30	0.390	1.33
6.84	0.1569	2.29	32.71	0.403	1.23
6.10	0.1569	2.57	36.71	0.446	1.22
5.46	0.1569	2.87	41.00	0.532	1.30
5.04	0.1569	3.11	44.43	0.600	1.35
4.84	0.1569	3.24	46.30	0.662	1.43

Summary of Results.

Water.—As the mean of two sets of concordant determinations, the constant of molecular elevation for water has been found to be 3.4.

Ethyl Alcohol.—The molecular elevation for ethyl alcohol is practically constant at 3.4 for all concentrations for which measurements have been made.

Propyl Alcohol.—For dilute solutions, 5 parts solute to 100 parts solvent, and under, the molecular elevation for propyl alcohol is practically identical with the constant for water and ethyl alcohol. With greater concentration the constant diminishes in value, reaching 2.75 for a solution containing 56.04 parts solute to 100 parts solvent.

Phenol.—In solutions of moderate concentration the molecular elevation of phenol is constant at about 3.0. With higher concentration the constant diminishes in value.

Pyrocatechin.—In solutions of moderate concentration pyrocatechin gives a molecular elevation of 3.2. With higher concentration the constant diminishes in value.

Resorcin.—The molecular elevation for resorcin is fairly constant for all concentrations for which measurements were made. The value of the constant is 3.5.

Hydroquinone.—Four sets of measurements were made on hydroquinone with not very satisfactory results. The mean values as calculated from the four sets of observations are, 3.8, 4.1, 3.5, and 3.7, respectively.

Sucrose.—Cane-sugar shows a fairly regular increase in the molecular elevation with rising concentration. Beginning with a value in the vicinity of 3.0 for the more dilute solutions, the molecular elevation increases in value until 4.7 is reached at a concentration of 75.79 parts solute per 100 parts solvent, the strongest solution measured.

Urea.—Beginning with a value approximately the same as that for water, the molecular elevation of urea diminishes with increasing concentration until a value of 2.26 is reached for a solution containing 26.53 parts solute to 100 parts solvent.

Pyridine.—In dilute solutions pyridine gives a molecular

elevation of about 3.2. With increasing concentration the molecular elevation was found to diminish in value. A solution containing 98.74 parts solute to 100 parts solvent, the strongest solution tested, gave an elevation of but 1.79.

Aniline.—The molecular elevation for aniline falls off somewhat with increasing concentration. The molecular elevation for dilute solutions seems to be greater than the constant for water. For the most concentrated solution upon which measurements were made, a solution containing 32.62 parts solute to 100 parts solvent, the molecular elevation was 3.12.

Acetic Acid.—Acetic acid reacts rather violently with ammonia, presumably forming ammonium acetate. The molecular elevation, however, which for moderate concentration was found to be about 2.0, decreasing to 1.58 for a solution containing 15.40 parts solute to 100 parts solvent, is calculated for acetic acid.

Orthonitrophenol.—Orthonitrophenol gives a molecular elevation distinctly larger than that given by phenol. The value is about 3.4.

Benzene.—For solutions of medium concentration, benzene produces a molecular elevation of about 2.5. In the more dilute solutions the elevation seems to be greater, reaching possibly a value above 3.0. Solutions of a concentration above about 12 parts solute to 100 parts solvent could not be tested because of the limited solubility of benzene in ammonia.

Salts.—Leaving out of consideration acetic acid and sodium acetate, we have so far measured the molecular elevation of but three salts, *viz.*, ammonium nitrate, sodium nitrate, and potassium iodide. Considering the fact that solutions of these salts in ammonia are good conductors of electricity, we expected to obtain values for the molecular elevation in the more dilute solutions very much higher than those actually measured. What may be the explanation of our apparently abnormal results; whether possibly the dissociation is really low, and the conductivity is made up by the higher velocity of a comparatively small number of ions, will have to be left

to the future to determine. Some experiments which show a rapid increase of the molecular conductivity of salt solutions with increasing dilution seem to indicate that possibly this explanation may be found to be the correct one. With the apparatus as used by us it is not possible to determine the molecular elevation of the boiling-point for very dilute solutions.

It seems reasonable to assume that the rapid rise of the molecular elevation with increasing concentration is due to the formation of a compound of ammonia with the salt.[1] It is interesting to note in this connection that if the solute, potassium iodide, be assumed to be in solution as $KI.7NH_3$, and the molecular elevation calculated in accordance with this assumption, then the values obtained for the successive measurements with the solution of potassium iodide, are respectively as follows: 1.59, 3.08, 3.49, 3.49, 3.56, 3.56, 3.53, 3.55, 3.55, 3.46, 3.49, 3.51, 3.61, 3.64, 4.51, 3.63, 3.67, 3.41, and 3.56.

Metallic Sodium and Metallic Lithium. — The very low molecular elevation for lithium and sodium, varying from 1.50 for the more concentrated solutions to about 2.30 for the more dilute, probably indicates the presence in solution of a molecule containing 2 atoms of the metal.[2]

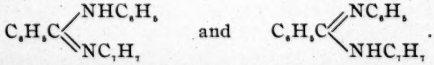
Contributions from the Sheffield Laboratory of Yale University.

LXVII.—ON THE NON-EXISTENCE OF FOUR METHENYLPHENYLPARATOLYL AMIDINES.

[SECOND PAPER.]

BY H. L. WHEELER AND T. B. JOHNSON.

It might be expected that amidines containing two different radicals attached to the different nitrogen groups would exist in more than one form. For example, theoretically, two structurally different benzenylphenylparatolyl amidines might exist:



[1] Ostwald: Lehrb. d. allgemein. Chem., p. 473.
[2] Joannis: Compt. rend., **115**, 820 (1898).

These, since they contain the grouping $(R)R'C{=}N-R''$, might be obtained in the form of geometrical isomerides.

In the case just cited Pechmann[1] believed that he obtained two isomeric amidines, when, by the action of aniline on benzparatolylimide chloride, he obtained an amidine melting at 133°, while from benzphenylimide chloride and paratoluidine an amide melting at 128° was formed. These two products were so much alike in properties and behavior that only the difference in the melting-points prevented the recognition of their identity. This doubt, however, disappeared when Marckwald[2] showed that the melting-points are practically identical when the amidines are crystallized from absolute alcohol. Moreover, the chlorides and picrates agree in melting-points. Pechmann[3] then thoroughly examined a number of mixed amidines, prepared by methods which, if the reacting substances reacted by double decomposition, would have yielded isomers, but he found that the resulting amidines were invariably obtained in only one form. Then followed the surprising result of R. Walther. He described the preparation of methenylphenylparatolyl amidine,

$$C_6H_5N{=}CH{-}NHC_7H_7 \quad \text{or} \quad C_6H_5NH{-}CH{=}NC_7H_7,$$

by four methods. Each method that he tried gave a new amidine, according to him, and these amidines were supposed to be isomers.

One of us was induced to examine Walther's products solely because his speculations, involving direct double decomposition, seemed incredible. The results obtained by crystallizing Walther's products have already been published.[4]

It was found that products melting near the temperatures given by Walther could be prepared, but these did not behave like pure substances, since on crystallizing a sufficient number of times the melting-points rose in each case. In one case (I. in table below) the melting-point finally coincided with that of methenyldiphenyl amidine. In another (II. in table below) with methenyldiparatolyl amidine. In the other

[1] Ber. d. chem. Ges., **27**, 1701. [2] Ann. Chem. (Liebig), **286**, 348.
[3] Ber. d. chem. Ges., **28**, 869, 2363; *Ibid*, **30**, 1779 and 1783.
[4] This JOURNAL, **19**, 367.

two cases (III. and IV.) the melting-points became almost identical.

Since these results appeared Zwingenberger and Walther[1] have again published the original paper with the addition of a more detailed account for the preparation of the different products and have added along with other material the melting-points of the salts they examined.

In this last article they admit that one of their products (III.) passes into the other (IV.), "durch Erhitzen in Petroläther." In spite of this fact, previously shown by one of us (they ignore the results obtained by crystallization), Zwingenberger and Walther still maintain that these compounds are different amidines and that four methenylphenylparatolyl amidines exist. The method of preparation of these products, the salts and melting-points, as found by these authors, are given in the following table:

Results of Zwingenberger and Walther.

	Preparation.	M. P. of product.	M. P. of $PtCl_4$ precipitate.	M. P. of picrate.
I.	By fusing together methenyldiphenyl amidine and *p*-toluidine.	120°	213°	178°
II.	By warming in alcohol methenyldi-*p*-tolylamidine and $C_6H_5NH_2.HCl$	132°	127°[2]	209°
III.	From formtoluide, aniline and PCl_5.	98°	207°	196°
IV.	From formanilide, *p*-toluidine and PCl_5.	102°	218°	193°

From the work done by one of us we knew that Walther's products I. and II. contained unaltered methenyldiphenyl and methenyldi-*p*-tolyl amidines respectively. It only remained to mix with these amidines what one might expect to get, *i. e.*, either one of the products obtained in III. or IV., to solve the mystery of the four methenylphenylparatolyl amidines.

Product, M. P. 120°.—By mixing 8 parts methenyldiphenyl

[1] Jour. prakt. chem., **57**, 209.

[2] Probably misprint in Z. and W.'s article, and is intended for 217°.

amidine (m. p. 135°) with 5.5 parts of methenylphenylparatolyl amidine (m. p. 98°–101°) and crystallizing this mixture once from petroleum ether, a product identical in every respect with the so-called methenylphenylparatolyl amidine of Zwingenberger and Walther can be prepared. The melting-point, behavior, appearance, all agree with the material prepared according to their directions, and the salts obtained from this mixture conform with surprising exactness with those prepared by the methods of Zwingenberger and Walther. (See I*a* in table below.)

Product, M. P. 132°.—By mixing 3 parts methenyldiparatolyl amidine (m. p. 140°) with 1 part of methenylphenylparatolyl amidine (m. p. 98°–101°), and crystallizing the mixture once from petroleum ether the so-called methenylphenylparatolyl amidine of Zwingenberger and Walther, melting at about 132°, can be obtained. The close agreement of these mixtures with the supposed amidines of Zwingenberger and Walther is shown by comparing the following table with I. and II. above:

Mixtures Prepared by Us.[1]

	M. P.	$PtCl_4$ precipitate.	Picrate.
I*a*. 8 parts methenyldiphenyl amidine and 5.5 parts methenylphenylparatolyl amidine.	119°–124°	213°	177°–178°

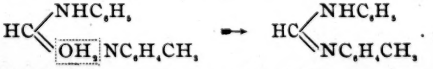
[1] It is unnecessary to describe here the various mixtures or proportions we experimented with. Within fairly wide limits the same results are obtained, so that the quantity of solvent is not given. A little more of the high-melting amidine raises the melting-point of the mixture while more of the compound melting at 98°–101° lowers the same. It is interesting to note that the lower-melting constituent that we used melts lower than the mixture in both cases; no evidence of melting could be detected in the mixture below the figures given, and, that while the product melting at 98°–101° usually separates from ligroïn or petroleum ether in the form of needles, nevertheless, when mixed with methenyldi-*p*-tolyl amidine, which separates in prisms, only the prisms form, at least at first. A product prepared according to Walther's fourth method, which usually forms prisms, melted at 105°. When mixed with methenyldiphenyl amidine gave needles melting at 120°–125°. We now have the explanation of Walther's results, in regard to the different crystalline forms of the products melting at 98° and 102°. The material simply contains small quantities of other amidines which not only affect the melting-point but determine what form shall result, either needles or prisms.

We will further examine these points later in other cases. What seems to be the best explanation of these curious facts is that the amidines form isomorphous mixtures, which, as experience teaches us, can only very slowly be separated by repeated crystallizations.

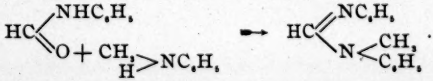
	M. P.	$PtCl_4$ precipitate.	Picrate.
IIa. 3 parts methenyldi-*p*-tolyl amidine and 1 part methenylphenylparatolyl amidine.	131°–133°	216°	209°

From this it is conclusively proved that Walther's amidines melting at 120° and 132° are mixtures and are therefore to be stricken from the literature. Since the same methenylphenylparatolyl amidine can be used in both of the above mixtures it follows that *only one mixed amidine results when Walther's first and second methods are followed.* When, in the above mixtures, in place of the product melting from 98°–101° the material prepared according to Walther's fourth method is used, almost the same melting-points are obtained both in the case of the duplicated "amidines" and their salts. It follows, therefore, that *these products obtained by the third and fourth methods contain the same amidine. That there is therefore no proof of a direct double decomposition in these reactions, and that at the present time only one methenylphenylparatolyl amidine is known.*

In closing it may be stated that Walther determines structure by the method of preparation of amidines[1] in spite of the fact that Pechmann has shown, in numerous cases, that this is impossible. He states that from formanilide, paratoluidine, and phosphorus trichloride the following amidine must be formed, $C_6H_5NH—CH=NC_6H_4CH_3$. In other words, the action, according to him, must take place as follows:



That the reaction does not proceed in this manner is shown by the fact that formanilide, methylaniline, and phosphorus trichloride give an excellent yield of methenylmethyldiphenyl amidine. Indeed, this appears to be a smoother reaction than when primary amines are used (see below):



[1] Jour. prakt. Chem., **55**, 43; *Ibid*, **57**, 229.

In this case it is impossible for the reaction to proceed as Walther states.

This reaction in the case of primary amines is altogether too violent to be used to decide delicate cases of isomerism. Indeed it takes place with such energy that it has never happened in our work that the products obtained by one and the same method show even approximate agreement in their melting-points on crystallizing the same number of times. In one case in an attempt to prepare Walther's amidine melting at 98°, a product was obtained, which, after seven crystallizations from ligroïn, did not melt above 86°. In another attempt to prepare Walther's product melting at 102°, the only approximately pure product we could isolate was an amidine crystallizing in prisms like methenylphenylparatolyl amidine. This, however, did not melt at 102°, after five crystallizations, but from 134°–135°. If the compound had separated in the form of needles it would have been identified as methenyldiphenyl amidine; it was, however, probably methenyldiparatolyl amidine, but the quantity was too small to enable us to decide this point. Again, in one preparation of the compound melting at 102° a product was obtained that melted at 105°.

The conclusion from these results is that Walther's amidines said to melt at 98° and 102° (none of his amidines as obtained by us, melted sharply), undoubtedly contain more or less of these impurities which caused the observed variations in melting-points.

Eight years ago it was found by Comstock and Wheeler, although the results were not published, that phenylformimidomethyl ester and metanitraniline gave the same methenylphenylmetanitrophenyl amidine as metanitrophenylformimidomethyl ester and aniline. Since these reactions take place at ordinary temperature this method of studying possible isomers here is by far the best that has yet been employed. We propose to prepare methenylphenyl-*p*-tolyl amidine by similar methods and determine how far the pure product differs from Walther's compounds.[1]

[1] Since the above was written we have prepared this amidine by these methods and find that it melts at 86°, and also that all the products described by Walther as methenylphenyl-*p*-tolyl amidines are, without exception, mixtures.

Methenylmethylphenylamide-phenylimidine, $C_6H_5(CH_3)N—CH=NC_6H_5$.—This amidine has been prepared now by three methods.

I. It was first obtained by Comstock and Wheeler[1] by mixing monomethylaniline with methylisoformanilide.

II. It has been obtained by us by adding a mixture of monomethylaniline and formanilide, in molecular proportions, to an excess of phosphorus trichloride. After the reaction the excess of phosphorus trichloride was poured off and the residue treated with pounded ice. On standing the material dissolved, and to the cold solution cold sodium hydroxide was added. This precipitated an amber-yellow oil, which was extracted with ether and dried over calcium chloride. The ether was then evaporated and the oil distilled at 25 mm. pressure. It began to boil at about 95°, then the temperature rapidly rose to 219°, when from 219°–220° all but a few drops of material was collected. The first portion contained unaltered (?) material while the portion boiling between 219°–220° consisted of almost pure amidine. From 10 grams of formanilide, 4.5 grams of low-boiling, and 12.1 grams of material boiling within one degree were obtained. The material thus obtained had a slight odor of phenylisonitril. It was redistilled at 30 mm. and again at 26 mm. pressure. That it was not decomposed by this treatment is shown by the fact that it boiled constantly at this pressure from 218°.5 to 219°. It still had an odor of isonitril, but this was present only in very small quantity.

III. In spite of the failures of Zwingenberger and Walther to prepare this amidine from methenyldiphenyl amidine by the action of methyl iodide, it can also be obtained in this way, but the preparation by this method is not to be recommended, as the yield, as determined by one experiment, is not good. We observed its formation when 10 grams of methenyldiphenylamidine were heated with an excess of methyl iodide to 135°–140° for seven hours. After evaporating off the excess of methyl iodide, a sticky colorless residue was obtained. This was shaken thoroughly with ether and water. The

[1] This JOURNAL, 13, 518; Beilstein [3], 2, 346.

ether took up the color and the aqueous solution was only pale yellow. A solid residue remained that did not dissolve. This proved to be the hydrogen iodide salt of unaltered amidine. The aqueous solution was treated with cold sodium hydrate, and the resulting oil separated, dried, and distilled at 30 mm. pressure; 2 grams of colorless oil came over below 226°, mostly dimethylaniline, then 3.5 grams of material, the greater portion distilled constantly at 226°, while above this 1.3 grams of thick oil remained. The portion boiling at 226° was not pure, however; it had the odor of isonitril, and deposited on standing, or, when treated with ligroïn, crystals of unaltered methenyldiphenyl amidine. The ligroïn solution gave the salts described below.

Methenylmethylphenylamide-phenylimidine prepared by any of these three methods is a pale yellow, almost colorless, oil which in a freezing-mixture (—15°) gets thick and pasty but could not be solidified. It is readily soluble in cold petroleum ether and the ordinary solvents. When concentrated hydrochloric acid is added to the oil it gives the solid hydrochloride.

The Hydrochloride, $C_{14}H_{14}N_2HCl$.—This is best prepared by dissolving the amidine in petroleum ether and passing in dry hydrogen chloride. The precipitate crystallizes from absolute alcohol in large transparent colorless rhombohedrons or thick tables. It melts with decomposition at about 228°. A chlorine determination in the same prepared from the material obtained by the second method gave:

	Calculated for $C_{14}H_{14}N_2HCl$.	Found.
Cl	14.4	14.3

This salt is very soluble in water and decomposes on standing in alcoholic solution.

The gold chloride double salt, $C_{14}H_{14}N_2HCl.AuCl_3$, has well-characterized properties and easily serves to identify the amidine. It separates from alcohol by adding water in yellow, six-sided plates with growth markings parallel to the edges. Prepared from material obtained by any of the above methods it melted sharply at 145° (as previously described). A por-

tion made from material obtained by the second method above gave the following result:

	Calculated for $C_{14}H_{14}N_2HCl.AuCl_3$.	Found.
Au(196.7)	35.7	35.3

NEW HAVEN, CONN., Oct. 20, 1898.

Contributions from the Laboratory of the North Dakota Agricultural College.

I.—AN ACTIVE PRINCIPLE IN MILLET HAY.

BY E. F. LADD.

As is well known among farmers, the exclusive feeding of millet (*Setaria Italica*) results in a diseased condition of horses which has come to be recognized as the "Millet Disease." One of the first symptoms is more frequent urination and an increased elimination. This feature is shown in case of the following animals—two horses. The daily average of urine for fourteen days when fed on hay was as follows:

	Urine per day. Grams.
Horse No. 1	7035.6
" " 2	5908.1

The same animals fed on millet gave the following daily average:

	Urine per day. Grams.
Horse No. 1	14404.9
" " 2	12258.0

The total solids in the urine averaged per day during the two periods:

	Hay fed. Grams.	Millet fed. Grams.
Horse No. 1	744.37	1127.9
" " 2	648.11	954.9

The urine contained of nitrogen on an average for the two periods:

	Hay fed. Grams.	Millet fed. Grams.
Horse No. 1	110.45	131.08
" " 2	90.39	121.35

These showed marked disturbance due to the action of some substance contained in the millet, and the continued use resulted in serious disturbances that have been described by Dr. Hinebauch.[1]

This work was undertaken to determine whether the millet hay contained an extractive principle capable of producing marked physiological disturbances, and to study the properties of the extract if such were found. For the present it became necessary to drop this work, and the results secured are herewith given with the expectation of investigating the subject more fully at some future time.

25 grams of the well-pulverized millet were treated in a separating-funnel for eight days with 250 cc. of petroleum ether. The product was then filtered and the filtrate evaporated to dryness. The total extractive residue amounted to 1.99 per cent. of the original millet.

The residue was then treated with 50 cc. of water slightly acidulated with sulphuric acid, for twenty-four hours, the filtrate was then transferred to a separating-funnel and agitated several times with ether to remove all fatty matter, and the aqueous solution preserved for testing.

The millet was again macerated for eight days in a separating-funnel with sulphuric ether, then filtered off, washed, and the extractive matter was found to be 0.86 per cent. of the millet. After treating the residue with 50 cc. of water slightly acidulated with sulphuric acid and allowing to stand for twenty-four hours, the aqueous extract was washed with ether and the water extract added to that previously secured from the petroleum extraction.

The millet was next macerated with alcohol for eight days and the extract evaporated to dryness over a water-bath. The total extractive matter was 6.53 per cent. of the millet. The ash was 0.28 per cent., leaving 6.25 per cent. of organic matter extracted by alcohol.

The extractive residue was then treated with 50 cc. of water and filtered off.

The extractive matter soluble in water taken out of millet

[1] North Dakota Experiment Station Bulletin No. 7.

by the petroleum spirits and by the sulphuric ether gave no reactions for any unusual active principle, and our attention was then turned to the alcoholic extract.

Reactions of the Solution of the Alcoholic Extract.

The aqueous solution of the alcoholic extract treated with alkalies gave no reaction. Treated with warm nitric acid there was no reaction. With concentrated sulphuric acid the solution became brown in color. When treated with a solution of gelatin and plumbic acetate a yellow precipitate formed at once. Copper acetate gave no reaction, indicating the absence of tannins. The solution was quite bitter to the taste, and suggested the presence of some alkaloid or glucoside. The aqueous solution of the alcoholic extract was then made slightly acid with sulphuric acid, and agitated successively with petroleum spirits, benzene, and chloroform. After each successive agitation with the above menstrua, the solvent was separated and washed with pure water, the product evaporated to dryness, and the residue carefully examined for any active principle. The results are given as follows:

Extracts from the Acid Solution.

Petroleum Spirit Extract.—A small quantity of oily product remains on evaporating the petroleum spirits extract. (As a check the petroleum spirits on evaporation gave no residue.) This product had an acrid odor and taste and was insoluble in water. The amount was too small for other tests.

Benzine Extract.—On evaporating the benzine extract there remained an oily liquid of a light-yellow color, solidifying slightly below the ordinary temperature of the laboratory. It had a disagreeable, irritant odor, turned brownish on the addition of concentrated sulphuric acid, yellow with nitric acid, and gave a green precipitate with Frohde's reagent. Carbolic acid gave a reddish-brown color; cane-sugar and sulphuric acid a violet color; potassium nitrate and sulphuric acid a yellow color; and with lead acetate a white precipitate was formed.

With the alkalies there was no reaction. When treated with acetyl chloride, the fumes being passed into a solution of argentic nitrate, a heavy precipitate was formed.

When treated with sulphuric acid the product was easily and quickly decomposed into a member of the glucose group capable of reducing copper from Fehling's solution.

Chloroform Extract.—A very small amount of material of a syrupy consistency remained on evaporating the chloroform extract. This product was nearly transparent, soluble in water, alcohol, and chloroform, but insoluble in petroleum spirits and benzine. On testing with hot dilute sulphuric acid it was converted into glucose. It is probable that this is a small portion of the same product as that described under the benzine extract, not fully removed by the treatment at that time.

A Glucoside.

The product extracted by benzine, as already described, is probably a glucoside. That it is not closely related to the tannins is shown by the negative reactions of the tests for tannins in the solution of the alcoholic residue before the separations were made. It has a bitter acrid taste and a pungent odor.

Of the glucosides with which I am familiar it most resembles daphnin, $C_{31}H_{34}O_{19}$, which is somewhat soluble in cold water, alcohol, and benzine, but insoluble in petroleum spirits. Daphnin is precipitated by plumbic acetate; acids resolve it into glucose, and alkalies color it yellow. In this last respect as well as in some others it differs wholly from the product we are dealing with. Daphnin is a bitter glucoside having a marked influence on the secretions, especially those of the skin and kidneys. Daphnin also forms colorless rectangular prisms when its aqueous solution is evaporated. The glucoside from millet hay forms no crystals when its water solution is evaporated, but an amorphous mass is left behind. That it is possessed of active physiological properties is indicated by experiments already mentioned, and that the product we have extracted and examined possesses this principle in a marked degree is shown by some experiments made by Mr. C. G. Warner, then a special student in my laboratory.

Physiological Action.

Some of the extract was prepared as indicated above, and the benzine extract, after separating it, as far as seemed possible, from other products, was then evaporated to dryness and again brought into solution with distilled water, and a series of experiments made upon mice, rats, and young cats to learn something of the effects of administering these products. To each of the animals were fed small quantities of the aqueous extract mixed with their food. In about two hours after feeding the reactions in each case were very marked upon all the animals under experiment. Urination was very frequent, every fifteen to twenty minutes, for some time, and the animals were stupefied as though from the action of some strong toxic product. The animals would stand upon their hind feet, their front feet stretched out before them, resting their nose upon the bottom of their pens, and, when forced to move about, they did so reluctantly and with a very unsteady gait, especially in their fore quarters. Of their hind legs they seemed to have pretty full use.

Hypodermic injections of the aqueous solution acted in the same manner, but more rapidly than when the extractive matter was administered with the food. Characteristic crystals were also formed with platinic chloride.

At this point Mr. Warner could no longer continue the work, and nothing more has since been done in this line.

Extracts from the Alkaline Solution.

The aqueous solution of the alcoholic extract, from which the acid extract (see above) had been prepared, was then made slightly alkaline and the agitation repeated as with the acid solution, petroleum spirits, benzine, and chloroform being used.

Nothing was separated or extracted by petroleum spirits or chloroform.

Benzine Extract.—A light-yellow, oily, and bitter liquid was removed by benzine from the alkaline solution. This product did not yield glucose by the action of sulphuric acid. The following color reactions were secured: Treated with

sulphuric acid it became dark-brown, gradually becoming lighter in color with the formation of a small precipitate. Frohde's reagent gave a dark-green color, sulphuric acid and cane-sugar gave a violet color, and with sulphuric acid and potassium bichromate it gave a peacock-blue color. Hydrochloric acid, nitric acid, ferric chloride, and sulphuric and nitric acids gave no reactions. It hardly seems probable that this product could be an alkaloid. It certainly is not a glucoside. Its physiological action was not studied, and lack of material prevented further tests at the time. At some future time it is proposed to continue this work, to prepare and purify the product, and to determine the composition and formula of the glucoside.

Much of the analytical work in the foregoing investigation was done by Mr. R. D. Ward, assisted by others who have been students in my laboratory.

AGRICULTURAL COLLEGE, N. DAK.,
August 29, 1898.

II.—COMPARISON OF METHODS FOR ESTIMATING CAFFEÏN.

BY E. F. LADD.

In making estimations of caffeïn it was necessary to make some comparative determinations of the value of different methods for the estimation of caffeïn in tea. Four methods were tried, Vite's, Peligot's, Crosschoff's, and Gomberg's. Briefly, the methods employed by us were as follows:

Vite's Method.—Five grams of the tea or other product, finely pulverized and extracted with 100 cc. of water, are kept at boiling for one hour, and then the solution decanted off. This extraction was repeated three times, and the combined filtrates concentrated on the water-bath to 75 cc. and mixed with freshly precipitated lead oxide and sand. The mixture is dried on a water-bath, powdered, and boiled with chloroform for three hours. The chloroform solution is then filtered off, evaporated to dryness, and the residue taken up in hot water. The clear aqueous solution is evaporated on the water-bath, dried at 100° C., and weighed.

Working on pure caffeïn by this method there was a loss of 10 per cent., and when working with tea in comparison with the other methods the loss was as much as 42 per cent. It seems that the caffeotannate is not wholly broken up by the lead oxide when working with samples of tea or coffee, and no further attempts were made to use this method.

Gomberg's Method.—The solutions necessary for this method are:

A solution of potassium iodide made by dissolving 18 grams of the pure salt and 12.65 grams of iodine in 250 cc. of water, and when dissolved diluting with distilled water to 1000 cc.

A solution of sodium thiosulphate made by dissolving 24.8 grams of the crystallized salt $Na_2SO_3.5H_2O$, in 1 liter of water. This solution is then standardized by means of a standard solution of potassium chromate, made by dissolving 4.913 grams in 1 liter of water. After the solution of the thiosulphate has been properly standardized by means of the solution of chromate, the solution of the iodide may be standardized by means of the standard sodium thiosulphate. The solution should then be kept in the dark.

The method, as employed, consists in boiling a definite quantity of tea, coffee, or other product with water, making up to a known volume, and then filtering. An aliquot portion is then treated with basic lead acetate as long as a precipitate is formed. After standing to allow the precipitate to settle, it is filtered off and the filtrate carefully treated with hydrogen sulphide to remove the excess of lead which is then filtered off. The filtrate is then boiled to drive off the excess of hydrogen sulphide and divided into two equal portions. One portion is acidified with sulphuric or hydrochloric acid, and each is then treated with a definite quantity of the standard solution of iodine. After allowing to settle for five or ten minutes it is filtered, and the filtrate treated with the standard tenth-normal solution of sodium thiosulphate.

The first solution without acid serves to show whether there is any product present that can be precipitated by Wagner's reagent. Should there be any, a corresponding correction will be necessary. One cc. of the sodium thiosulphate corresponds to 0.00485 gram of caffeïn.

By this method, working with 0.1 gram and 0.2 gram of pure caffeïn, 99.9 and 100.5 per cent., respectively, of caffeïn were removed, showing most excellent results; and, when working on teas, higher and apparently more nearly accurate results were obtained than by either of the other methods.

Peligot's Method.—Ten grams of tea were weighed out and 250 cc. of water at 100° C., added and allowed to stand for fifteen minutes. This is then filtered through a fine cloth and a solution of basic lead acetate added to precipitate all the tannin, the precipitate allowed to settle, and then filtered. The filtrate is then treated with hydrogen sulphide to remove all excess of lead. The solution is then filtered off, the filtrate evaporated to dryness, and weighed. An excess of lead and prolonged treatment with hydrogen sulphide results in diminished amount of caffeïn, possibly from the action of the sulphide on the caffeïn. Working with pure caffeïn the results agree closely with those obtained by Gomberg's method.

Crosschoff's Method.—A decoction is made with 1 ounce of tea and 600 to 1000 cc. of cold water. The temperature is then gradually raised to boiling, and the solution allowed to stand for a few minutes, when it is filtered through a cloth. About 3 grams lead oxide is added to the filtrate, and it is made alkaline by the addition of potassium chlorate. This is allowed to stand for a few hours, and then it is evaporated to a syrup. The caffeïn is dissolved out with about 400 cc. of alcohol, the solution filtered, the alcohol evaporated off, and the caffeïn allowed to crystallize. The crystals are redissolved in alcohol, the solution passed through a charcoal filter, and evaporated to crystallization. The residue is then dried and weighed.

With pure caffeïn good results were obtained by this method. The following table gives results secured with three samples of tea by these methods:

Per Cent. of Caffeïn Found.

	Kind of tea.		
Method.	Congo.	Green tea.	Gunpowder.
Peligot	0.843	2.061	3.680
Crosschoff	0.919	2.031	3.200
Gomberg	1.542	2.386	3.986

It will be seen that higher results were uniformly secured working with Gomberg's method than by either of the others and its simplicity makes it the most desirable method for rapid work where caffein has to be determined.

The analytical work has all been performed by Mr. Benn, a senior student in my laboratory.

AGRICULTURAL COLLEGE, N. D.,
July 29, 1898.

III.—CREATIN AND ITS SEPARATION.

BY E. F. LADD AND P. B. BOTTENFIELD.

In some work on the alloxuric bodies resulting from metabolism undertaken by one of us (E. F. L.), it was found desirable to make some investigation relating to creatin and to be able to determine and identify it. For that purpose a comparison of the principal methods employed in its determination was undertaken, and the final results as secured by one of us (P. B. B.) are here presented for the purpose of showing the value of the methods for the conditions under which we were obliged to work. The three methods employed were Neubauer's, Liebig's, and Stradeler's, the determinations being made as follows:

Neubauer's Method.—The meat is first cut into very small pieces by running it through a sausage machine. 700 grams of this product were then extracted for ten to fifteen minutes with an equal weight of water at 55°–60° C. It is then pressed with a screw-press and again extracted as before with water. The two extracts united are then heated to boiling to coagulate the albumin. After filtering, the filtrate is treated with basic lead acetate as long as a precipitate forms; the excess of lead is then removed from the filtrate by hydrogen sulphide. The filtrate is now carefully concentrated to a small volume on the water-bath, and then allowed to stand for several days to allow the creatin to crystallize. The crystals of creatin are now collected on a filter-paper and well washed with alcohol. The crystals thus secured are redissolved, filtered through charcoal, and again recrystallized, well washed with alcohol, dried, and weighed.

Liebig's Method.—The product is reduced to a fine state of division, in case of meat, by passing through a sausage machine, and then extracted with one-half its weight of cold water for a few hours, then pressed with a screw-press, and again extracted in the same manner with cold water. The two filtrates united are heated to boiling to coagulate the albumin, and to the filtrate baryta water is added to remove the phosphates. The excess of barium is then removed by carbon dioxide. After filtering and washing, the filtrate is evaporated on a water-bath to a syrupy consistency, and then allowed to stand for several days so that all the creatin may crystallize out. The crystals are then removed, washed with alcohol, and purified as in Neubauer's method.

Stradeler's Method.—The finely divided material is digested on the water-bath with twice its volume of alcohol for several hours, then pressed as in the preceding methods. The filtrate is evaporated to a small volume. A solution of basic lead acetate is then added as long as a precipitate is formed, and the process continued as in Neubauer's method.

Samples of flesh from an ox and from a dog were treated by these three methods with results as presented below:

Per Cent. of Creatin.

	Neubauer's.	Stradeler's.	Liebig's.
Ox	0.250	0.234	0.215
Dog	0.242	0.230	0.218

Voit in his experiments found in the flesh of the ox from 0.219 to 0.276 per cent. of creatin, and in the flesh of the dog the same investigator found from 0.223 to 0.248 per cent.

It will be seen that the above results are in accord with those found by Voit for the same animals. The method of Neubauer gives results somewhat higher than those by the method of Stradeler or that of Liebig.

In Liebig's method there are several sources of error. The use of cold water does not leave the meat in as good condition as in Neubauer's method, and it is impossible to press the meat as dry. Again we were not able to remove all traces of the barium by means of carbon dioxide without some loss of creatin. The use of alcohol in Stradeler's method results in extracting some of the fats and other products, and a re-

moval of these products results in some loss of creatin, but this is not as great as in Liebig's method.

AGRICULTURAL COLLEGE, N. D.,
August 7, 1898.

A DOUBLE CITRATE OF ZIRCONIUM AND AMMONIUM.

BY S. H. HARRIS.

The chlorides of zirconium used were those obtained by dissolving zirconium hydroxide, $Zr(OH)_4$, in concentrated hydrochloric acid, and repeatedly crystallizing from the same. The mixed chlorides were then recrystallized from water. A portion of the mixed chlorides was dissolved in eight to ten times as much water. To this was added an aqueous solution of ammonium citrate (1–5) drop by drop, with constant stirring, until the precipitate ceased to form. The precipitate comes down as a white, curdy mass, and is very easily soluble in even a slight excess, so that great care must be exercised. When the maximum amount of precipitation had occurred, hot water was added and the mass filtered off on a large plain filter. The precipitate was then washed back into the beaker with hot water, well stirred up and filtered again. After two or three more such washings the filter-paper containing the precipitate was spread open to dry on an unglazed porcelain plate. When dry it was pulverized, placed on a watch-glass, and heated to 100° C. in an air-bath for several hours. The substance proved to be very deliquescent; so much so that it could not be weighed in an open glass. It was then placed in a weighing-bottle and heated in an air-bath at 100° C. for six hours, the stopper replaced quickly, and weighed. During the intervals between the heatings the weighing-bottle containing the double salt was kept in a desiccator over concentrated sulphuric acid.

No. of heating.	Hours.	Temperature.	Wt. bottle + citrate. Grams.	Moisture driven off. Gram.
1	6	100°	24.5916	....
2	6	110°	24.5211	0.0705
3	6	120°	24.4465	0.0746
4	6	120°	24.4151	0.0314
5	6	120°	24.4108	0.0053
6	6	120°	24.4108	0.0000

Here the heating was stopped, as the substance lost no more water, and seemed to have come to a constant weight. A small portion of the substance was ignited in a platinum crucible. It chars at first, showing the presence of citric acid, and on complete ignition leaves a white residue of zirconium oxide, ZrO_2. The ammonia is held very firmly in combination, and can only be driven off by boiling with a solution of sodium hydroxide.

Estimation of Zirconium.—The double citrate, after the drying previously described, was poured out of the previously weighed weighing-bottle into a large platinum crucible, as quickly as possible, the stopper replaced, and the bottle weighed again. The crucible was then heated on a sand-bath until it had charred and the combustion slowly and cautiously completed with a Bunsen burner until the residue of zirconium oxide was perfectly white. For this analysis 0.626 gram of the citrate was taken. I found $ZrO_2 = 0.3593$ gram, which, taking the atomic weight of $Zr = 90.6$, gives 0.2655 gram Zr, or 42.40 per cent. Zr.

Attempt to Estimate Citric Acid.—For this analysis 1.9705 grams were taken. An attempt was made to dissolve this in dilute sulphuric acid (1–20), but the citrate was only very slightly attacked, even when the acid was heated to boiling. The liquid was filtered off, however, from the unchanged citrate and titrated in a porcelain dish at 60°–70° C., against a standard solution of potassium permanganate, but only 14 cc. were necessary, showing that very little of the citrate had been attacked. It is impossible to get the substance to dissolve without decomposition, and hence the citric acid determination had to be abandoned. This being the only available method with this particular substance, it was impossible to determine the citric acid.

Estimation of Ammonia.—A portion of the citrate was analyzed by the Kjeldahl method for ammonia and 11.92 per cent. found. The formula $Zr_2(C_6H_4O_7)(NH_4)_2$ agrees fairly well with the results obtained for zirconium and ammonia.

	Calculated.	Found.
Zr	42.71	42.40
NH_3	12.02	11.92

NOTE.

Xenon, Etherion, and Monium.

In a note in a recent number[1] of this JOURNAL the methods used by Ramsay for the isolation of krypton, neon, and metargon were described. Since the publication of that paper another gas has been added to the number of those obtained from the liquefied argon. This gas, to which the name "xenon" has been given, can be readily separated from the others as it has a higher boiling-point and remains behind after the others have evaporated. Its spectrum is analogous to that of argon; but the lines occupy a different position in the spectrum and the colors vary according to the methods used to produce the discharge. All these gases exist only in minute quantities, the amount of neon being about 1 part to 40,000 of air.

At the summer meeting of the American Association for the Advancement of Science a paper entitled "A New Gas" was read by Mr. Chas. F. Brush. During an investigation of the heat conductivity of gases at different pressures the author found that a substance could be extracted, at low pressures, from glass, and that the behavior of the substance thus extracted was entirely different from that of all known gases. By heating pulverized glass he obtained a gas which had a heat conductivity, at a pressure of 0.12 of a millionth, forty-two times that of hydrogen. This gas, which is present in the air, is absorbed by many substances; but especially by glass, and the supply of the gas in the glass can be renewed by exposing the glass to the air. He can separate the gas from other substances, to a considerable extent, by diffusion through a porous porcelain tube, and he considers from the results already obtained, the value 100 as a fair one for the relative heat conductivity of the pure gas, if hydrogen = 1. From this the molecular velocity was calculated and the result showed a velocity of 105 miles per second. On the basis of this the density would be 0.0001 if H = 1, and the molecular weight would be 0.0002. The great velocity would make it impossible for this gas to remain in the atmosphere unless the space above also contained it. The author suggests that perhaps this is the ether of the physicist to which such remarkable properties have been ascribed, and he suggests the name "etherion" for it.

In *The Chemical News* of Nov. 4, 1898, there is an article by Sir William Crookes in which he describes some experiments that lead him to "consider it more probable that etherion is water vapour than that it is a new elementary gas."

Sir William Crookes, who has been working for a number of

[1] This JOURNAL, **20**, 696.

years on the separation of the constituents of yttria, has isolated a new elementary substance from this material. By skilful methods of fractionation, using a specially designed form of the spectroscope to test the relative amounts of the substances present, he has isolated a substance which gives a characteristic series of lines at the extreme end of the ultra-violet spectrum. He has given it the name "Monium" from the Greek word for "alone." This substance, unlike the gases discovered by Ramsay, readily forms compounds with other elements, and although the details of the investigation have not yet been published, the author states that the atomic weight will be very close to 118. J. E. G.

REVIEWS.

LEHRBUCH DER ANORGANISCHEN CHEMIE. By DR. HUGO ERDMANN, Professor in the University of Halle. Braunschweig: F. Vieweg und Sohn. 1898. pp. xxvi, 756.

Any one who is familiar with Professor Erdmann's useful little book on the preparation of inorganic compounds will at once welcome the idea of a larger work from the same pen. It is a pleasure to say that this new volume will not disappoint such expectations. Considering its size, the book is an unusually comprehensive treatise upon the experimental side of modern inorganic chemistry, and the reader is attracted by the scope of the writer's knowledge, as well as by his ability in compressing this knowledge into clear, concise, readable language. Some text-books endeavor to express a great deal in a few pages by systems of abbreviation, but Professor Erdmann has avoided this unfortunate method. He has adopted two sizes of type, and a system of useful marginal references, which enable one to read in an uninterrupted manner either the salient features, or the less important details, or both, as the reader may wish; and has illustrated his book by an unusually large number of good wood-cuts and three remarkably brilliant plates of spectra. The arrangement is, of course, based primarily on the periodic system, after an introduction containing an essay on measurement, number, and the general principles of physics which underlie chemical phenomena. One is rather surprised to find the description of the periodic system itself at the very end, where also are to be found the scanty pages devoted to the hypothesis of electrolytic dissociation. In view of this latter circumstance, one cannot but regret that more ancient theories have been treated almost as facts; indeed the book is hopelessly old-fashioned on the theoretical side. Since, however, it does not pretend to be a treatise on theoretical chemistry, the lack of

prominence given to modern generalizations may perhaps be pardoned, and one should turn rather to the treatment of the facts. Here especial emphasis is laid upon recent discoveries, and upon all those chemical relations which are most intimately connected with the life of man. The organisms of nitrification, argon, helium, liquid air, fluorine, the electric furnace and the carbides, as well as the Welsbach light, all receive satisfactory treatment; and the historical, economic, and toxicological details throughout are apropos and interesting. Even krypton, neon, and metargon find a place in a note at the conclusion.

Of course, an occasional inaccuracy in such a work is inevitable, but one regrets to find the book marred by a large number of mistakes. The change from an old standard of reference to a new one is a process fraught with possibilities of error, and Professor Erdmann, in the premature use of hydrogen instead of oxygen as a standard of atomic weights, has not escaped an occasional lapse. One is not much surprised, for example, to find that the specific gravity of air referred to hydrogen is given at 14.44. More surprising is his history of the discovery of helium, in which the name of Ramsay does not appear; that of nitrogen chloride, from which Gattermann's name is omitted; and that of the atomic weight of oxygen, where the value 15.88 is ascribed to Keiser, without mention of the name of Morley. Distilled dilute nitric acid should certainly not be called $N(OH)_3$, because it happens to contain about 36 per cent. of water. In the explanation of the economy of the atmosphere, the fact that the absorption of carbon dioxide by plants is a process of assimilation and not of respiration, and that most plants, in common with other organisms, require oxygen to sustain life, is not made clear. The table of magnitudes given at the end, while compassing the distances of the fixed stars as well as the size of the hydrogen atom, is not adapted to assist the average imagination in either direction. But in spite of these and other deficiencies, the book is so full of admirable material that it will undoubtedly serve a very useful purpose, especially as an experimental guide to the teacher of the facts of inorganic chemistry.

T. W. R.

INORGANIC CHEMISTRY ACCORDING TO THE PERIODIC LAW. By F. P. VENABLE, University of North Carolina, and JAS. LEWIS HOWE, Washington and Lee University. Easton, Pa.: The Chemical Publishing Company. 1898. pp. 266. Price, $1.50.

In preparing their book the authors have followed the advice given by Lothar Meyer in his lecture before the German Chemical Society, and "have made the experiment of a com-

plete and faithful introduction'' of the system recommended by him. They say: ''In no other way have we been able to secure such excellent results both as to thorough systematic instruction and economy of time.'' The matter is presented in the order below indicated:

PART I.—Introduction; Definitions; Nomenclature; System; Laws.

PART II.—The Elements: Their History, Occurrence, Preparation, Properties.

PART III.—The Compounds of the Elements with Hydrogen, or Hydrids.

PART IV.—The Compounds of the Elements with the Halogens, or Halids.

PART V.—The Compounds of the Elements with Oxygen, or Oxids; the Compounds with Sulphur, or Sulphids; Selenium; Tellurids.

PART VI.—The Nitrids, Phosphids, Carbids, Silicids, and the Alloys.

At the end of PART I we find this paragraph: ''This introduction contains, in outline, some of the great principles of the science. It is scarcely expected that they will be fully grasped and comprehended by the student just entering upon the study. He is rather to look upon much of it as a statement of what is to be proved by his further study. A good deal will be repeated in suitable places later when the facts have been acquired which will render explanation possible. It is scarcely practicable to start upon the study of the science without some such frame-work for the building.''

If instead of saying ''it is scarcely expected that they will be fully grasped and comprehended by the student just entering upon the study'' the authors had used the stronger expression: ''It is certain that the student just entering upon the study will not comprehend what has gone before,'' they would have stated what every experienced teacher knows to be true. A college president once said to a teacher of biology: ''I suppose you will begin your course by a statement of the general principles of the science.'' The teacher answered: ''No, I shall begin with a bushel of clams.'' That teacher had been trained by Agassiz, and knew how to teach.

It is impossible to judge of the merits of a method of presentation without trying it, and the writer of this notice, while admitting that the plan suggested by Lothar Meyer and followed by the authors of this book does not commend itself to him, is willing to admit that his judgment may be at fault. Let those who feel otherwise try the book and judge it by the results.

As far as the contents of the book are concerned, leaving out of consideration the plan, it need hardly be said that they give evidence of scholarship on the part of the authors, and that there is much in the book that merits commendation.

I. R.

JAHRBUCH DER CHEMIE. Bericht über die wichtigsten Fortschritte der reinen und angewandten Chemie. Unter Mitwirkung von H. BECKURTS (Braunschweig), C. A. BISCHOFF (Riga), E. F. DÜRRÉ (Aachen), J. M. EDER (Wien), R. FRIEDLÄNDER (Wien), C. HÄUSSERMANN (Stuttgart), F. W. KÜSTER (Göttingen), J. LEWKOWITSCH (Manchester), M. MÄRCKER (Halle), F. RÖHMANN (Breslau), K. SEUBERT (Hannover), herausgegeben von RICHARD MEYER (Braunschweig). VII Jahrgang. 1897. Braunschweig: Druck und Verlag von Friederich Vieweg und Sohn. 1898.

Attention has been called to this excellent publication year after year since the appearance of the first volume in 1891. Here is the seventh volume. "Good wine needs no bush;" and this is in fact "good wine." Even the best-read chemist will find the book profitable. If he will from time to time during the year "finger the pages" he will be sure to be rewarded by finding clear and concise reports of articles which he may have read at the time of their publication, and also of some that may have escaped his serious attention. It is a good book to have at hand for frequent reference, even though one has also the more elaborate *Centralblatt*.

I. R.

TEXT-BOOK OF MEDICAL AND PHARMACEUTICAL CHEMISTRY. By ELIAS H. BARTLEY, B.S., M.D., PH.G., Professor of Chemistry and Toxicology in Long Island College Hospital, etc. Fifth edition. Revised and enlarged. Philadelphia: P. Blakiston's Son & Co. 1898. 738 pp. Price, $3.00.

That medical students ought to know something about chemistry no one will deny. That they are not likely to learn much about it after entering the medical school most will admit. The conditions are there unfavorable, and necessarily so, for the study of any one of the fundamental sciences. The students are interested in matters that pertain directly to the practical side of medicine, and have no time to dwell upon chemical phenomena as such to a sufficient extent to reach a comprehension of the simplest of these. It would be best for them to get their chemistry before going to the medical school and, as is well known, efforts are being made in various places to secure this. But here again, how much chemistry can one acquire in a year's course even under the best of circumstances? Let those who have tried the experiment make answer.

All this is suggested by the book of the above title. As long as the present conditions continue, it will probably be neces-

sary to have books of this kind that give a little physics, more chemistry, and considerable pharmacy, with a touch of physiology. One cannot help pitying the student who is expected to master the contents of the book. If he should succeed he would have "all the chemistry that every educated doctor ought to know" and a great deal more. He would be especially qualified to revel in constitutional formulas. To be sure, he might find it difficult to tell what they mean, but this is true of some chemists. A great and good bishop once said to the writer: "I imagine any man would be much surprised if he could learn just what idea of God is entertained by his neighbor." Surprise would probably give way to utter astonishment if one could learn what idea of pinene, terpinin, terpin, and terpin hydrate is entertained by the student who has studied page 324 of this book. In introducing the benzene series the author says: "The compounds of this series differ from all others thus far mentioned in the structure of their molecules in that the carbon atoms are arranged in the form of a closed chain, or cycle, at the angles of a regular hexagon." That statement is definite enough. The carbon atoms are at the angles of a regular hexagon. What idea does that convey to the medical student? The plot thickens as we advance. If there is one substance above another that it behooves a medical student to study, it is albumin. By the time he reaches page 515 he will be pleased to learn about the hemi-group and the anti-group; the hemi-proto and the anti-proto; hemi-deutero and the anti-deutero albumoses. And so on to the end.

In general, the presentation is clear, but it appears to the writer that the author has attempted too much if this book is intended for medical students. It may serve a useful purpose as a book of reference for the practitioner. But there is much in the purely scientific parts that needs modification.

I. R.

SOAPS. A practical manual of the manufacture of domestic, toilet and other soaps. BY GEORGE H. HURST, F.C.S. London: Scott, Greenwood, & Co., and New York: D. Van Nostrand Company. 385 pp. Price, $5.00.

In his preface the author says: "The substance of this book has already appeared in the form of articles in the pages of the *Oil and Colourman's Journal*. These articles were received with so much favor by the readers of that Journal that it has been thought desirable to collect them together and reprint them in book form. For this purpose the articles have been thoroughly revised and new matter added to bring the subject up to date. The author has not attempted to write a

complete treatise on soap manufacture, but has aimed at presenting in a brief but, it is hoped, clear manner the principal processes of soap manufacture, with an account of the raw materials used and the scientific principles which underlie the various operations."

The book is made up of ten chapters in which the following subjects are presented: I. *Introductory:* Soap, Nature of Soap, Action of Soap; II. *Soap-makers' Alkalies*; III. *Soap Fats and Oils;* IV. *Perfumes;* V. *Water as a Soap Material;* VI. *Soap Machinery;* VII. *Technology of Soap-making;* VIII. *Glycerine in Soap Lyes;* IX. *Laying Out of a Soap Factory;* X. *Soap Analysis.* The treatment is clear and the book carries upon its surface the evidence that the writer knows his subject. The important experiments of F. Krafft on the action of soap seem to have escaped the notice of the author.

MANUAL OF DETERMINATIVE MINERALOGY WITH AN INTRODUCTION ON BLOWPIPE ANALYSIS. By GEORGE J. BRUSH, Revised and enlarged, with entirely new tables for the identification of minerals by SAMUEL L. PENFIELD. Fifteenth edition. New York: John Wiley & Sons. 1898. 312 pp. 8vo. Price, $3.50.

The appearance of this book marks the completion of a revision of this well-known and highly valued text-book which first appeared in 1874. Although the work has reached its fifteenth edition, few changes were made in text or tables until 1896. At this time the first 150 pages appeared in a rewritten and enlarged form that increased the value of the book by the introduction of new tests of decisive and practical character—by the simplification of previous methods and by the addition of many helpful suggestions based on Professor Penfield's experience as a teacher and as an investigator. The new analysis of the presentation and the revised phraseology in the descriptions of methods and apparatus also add much to the clearness of the treatment.

The edition which has just been issued removes one of the two glaring defects in the preceding issue. The tables are revised but the same lack of finish in the art of book-making remains. It seems a shame that text of such high order should be presented to the reader on such poor paper and accompanied by such imperfect figures. Neither of the latter is at all in keeping with the price of the book or the usage to which it must be subjected.

Two features are of especial value in the present editions—the added chapter on the physical properties of minerals and the revised tables. In the first the crystallographic treatment is marked by the acceptance of the recent classification of

forms into thirty-two classes and the rejection of all systems of notation except that of indices. Although certain of the classes are omitted the general discussion is characterized by its balance and its concise, clear descriptions of those mentioned. This chapter will prove valuable to chemists and mineralogists who desire a short presentation of crystal symmetry from the point of view which is accepted at the present time. It also offers succinct descriptions of the methods of determining the specific gravity and the purity of mineral fragments by means of heavy solutions.

The determinative tables are newly prepared on the same general plan as that employed in previous editions and are brought up to date by the insertion of many new minerals and more approved and more distinctive tests for previously recognized species. The total number of minerals included reaches full 800 and the relative importance is indicated by differences in the type.

E. B. MATHEWS.